Supporting information

Bismuth(III) forms exceptionally strong complexes with natural organic matter

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S1
Coordination chemistry of bismuth(III)

Bismuth(III) exhibits a broad range of coordination numbers from 3 to 10 in complexes and coordination compounds (Table S4). The coordination chemistry of bismuth(III) is strongly influenced by its electron configuration, $5d^{10}6s^2$, and show an unusual diversity. The tendency of the heavier main group elements to adopt an oxidation state two steps below being fully oxidized was originally attributed to the effect of the so-called “inert electron-pair”. This property was explained by the relativistic stabilization of the 6s orbital, caused by the direct relativistic effect and the presence of the filled 4f subshell. According to the valence bond theory, the inert electron-pair can either occupy a hybrid orbital formed by mixing the 6s and 6p orbitals on the metal ion and as such becoming stereochemically active, or be a pure s$^2$ electron-pair and thereby stereochemically inactive. The hybrid orbital with a lone electron-pair can in terms of coordination number be considered as at least an additional ligand in the coordination sphere normally taking up more space than that of an ordinary ligand. However, according to molecular orbital theory the classical concept of 6s/6p orbital hybridization on the isoelectronic lead(II) ion is regarded as incorrect as the energy level of these orbitals are too different and the very different spatial distribution of their wave-functions. This should certainly also apply for the isoelectronic bismuth(III) ion as it displays a similar kind of coordination chemistry as lead(II) and thallium(I). The coordination chemistry of lead(II) and bismuth(III) is not expected to be identical as the higher charge of latter will favor higher coordination numbers due stronger electrostatic bonds. The strong stereo-chemical activity observed in a large number of bismuth(III) complexes must instead be a result of an anti-bonding bismuth 6s-ligand np (6s/np) interaction which cause structural distortions in order to energetically minimize these unfavorable covalent interactions. Two general structural types of bismuth(III) complexes can be identified, i/ complexes with high symmetry and high coordination numbers, 8-10, in basical square antiprismatic, tricapped trigonal prismatic and bicapped antiprismatic fashion, respectively, ii/ complexes with a severely distorted coordination sphere with large difference between the shortest and longest Bi-O bond distance and generally with a clearly visible gap in the coordination sphere. The six-coordinated complexes can be regarded as distorted eight-coordinated ones with a gap taking up the same space as two ligands where the strongly bound ligands form a 3-legged stool. Between these and the gap are three more ligands much more weakly bound, or a distorted pentagonal pyramidal configuration with a much shorter Bi-O bond distance to the ligand in the apex than to the remaining three ones. Seven-coordinated complexes have either
distorted monocapped octahedral or bicapped pentagonal configuration both displaying a significant gap in the coordination sphere. The mean Bi-O bond distances are dependent on both coordination number and geometry as summarized in Table S4.

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Redox chemistry of bismuth

Bismuth has four oxidation states with known chemistry, metallic bismuth, bismuth(I) (d\(^{10}\)s\(^2\)p\(^2\) electron configuration), bismuth(III) (d\(^{10}\)s\(^2\)) and bismuth(V) (d\(^{10}\)). The most stable oxidized form of bismuth is the oxidation state +III. Metallic bismuth \textit{versus} bismuth(III) has a positive standard electrode potential, +0.308 V, see Table. Therefore, it does not react with non-oxidizing acids such as hydrochloric acid, but oxygen in air will until a protective layer of Bi$_2$O$_3$ is formed. Bismuth(I) is uncommon oxidation state, but it is stabilized is solvents binding through covalent interactions forming e.g. an unusual dimeric solvate complex in the solvent N,N-dimethylthioformamide (dmf), [Bi$_2$(dmf)]\(^{2+}\). Bismuth(V) is a very strong oxidizing agent and is easily reduced to bismuth(III). Bismuth(V) has no known aqueous chemistry.

Table. Standard electrode potentials of some bismuth redox couples from ref. 1.

| Redox couple | E\(^0\)/V |
|--------------|-----------|
| Bi\(^+\)(aq) + e\(^-\) $\rightleftharpoons$ Bi(s) | 0.5 |
| Bi\(^{3+}\)(aq) + 3e\(^-\) $\rightleftharpoons$ Bi(s) | 0.308 |
| Bi\(^{3+}\)(aq) + 2e\(^-\) $\rightleftharpoons$ Bi\(^+\)(aq) | 0.2 |
| Bi$_2$O$_3$(s) + 3H$_2$O + 6e\(^-\) $\rightleftharpoons$ 2Bi(s) + 6 OH\(^-\)(aq) | -0.46 |

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Table S1. Summary of stability constants of the formation of the complexes BiOH$^{2+}$ ($K_1$), Bi(OH)$_2^+$ ($\beta_2$) and Bi$_6$(OH)$_{12}^{6+}$ (equivalent to [Bi$_6$O$_4$(OH)$_4$]$^{6+}$)($\beta_{6,12}$) in aqueous solution.

| $K_1$  | $\beta_2$ | log $\beta_{6,12}$ | Temp | Ionic medium   | Ref. |
|-------|-----------|--------------------|------|----------------|------|
| 12.42 | 168.33    | 298                | 3.0 mol·dm$^{-3}$ NaClO$_4$ | 1    |
| 12.42 | 168.33    | 310                | 0.15 mol·dm$^{-3}$ NaClO$_4$ | 2    |
| 12.6  | 25.8      | 298                | 0.25 mol·dm$^{-3}$ NaClO$_4$ | 3    |
| 12.0  |           | 298                | 1.0 mol·dm$^{-3}$ NaClO$_4$  | 4    |
| 12.55 | 26.13     | 295                | 0.10 mol·dm$^{-3}$ KNO$_3$   | 5    |
| 12.36 |           | 298                | 0.10 mol·dm$^{-3}$ NaClO$_4$ | 6    |
|       |           |                    | 1.0 mol·dm$^{-3}$ NaClO$_4$  | 7    |

$K_1$=[BiOH$^{2+}$]/[Bi$^{3+}$][OH$^-$]; $\beta_2$=[Bi(OH)$_2^+$]/[Bi$^{3+}$][OH$^-$]$^2$; $\beta_{6,12}$=[Bi$_6$(OH)$_{12}^{6+}$]/[Bi$^{3+}$]$^6$[OH$^-$]$^{12}$

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Table S2. Selected stoichiometric stepwise stability constants, $K_n$, of bismuth(III) complexes with organic ligands in aqueous solution. \( K_1 = \frac{[\text{BiL}^{(3-x)^+}]}{[\text{Bi}^{3+}][\text{L}^{x-}]} \); \( K_2 = \frac{[\text{BiL}_2^{(3-2x)^+}]}{[\text{BiL}^{(3-x)^+}][\text{L}^{x-}]} \); \( K_3 = \frac{[\text{BiL}_3^{(3-3x)^+}]}{[\text{BiL}^{(3-2x)^+}][\text{L}^{x-}]} \).

| Ligand            | Bind. atoms | $\log_{10} K_1$ | $\log_{10} K_2$ | $\log_{10} K_3$ | Ionic medium | Temp. | Ref. |
|-------------------|-------------|-----------------|-----------------|-----------------|--------------|-------|------|
| Oxalic acid       | 2O          | 7.65            | 4.81            |                 | 0.2 M NaClO₄ | 25 °C | 1    |
| Glycine           | NO          | 10.0            |                 |                 | 0.5 M        | 25 °C | 2    |
| Malonic acid      | 2O          |                 |                 | $\beta_2=11.20$ | 0.1 M KNO₃  | 25 °C | 3    |
| Cysteine          | NO(S)       | 16.2            |                 |                 | 0.5 M NaClO₄ | 25 °C | 4    |
| Fumaric acid      | 2O          | 6.70            |                 |                 | 0.2 M NaClO₄ | 25 °C | 1    |
| Succinic acid     | 2O          | 8.76            |                 |                 | 0.2 M NaClO₄ | 25 °C | 1    |
|                   |             |                 |                 | $\beta_2=11.60$ | 0.1 M KNO₃  | 25 °C | 3    |
| Malic acid        | 2O          | 9.90            |                 |                 | 25 °C        | 5     |
| Diglycolic acid   | 3O          | 7.69            | 5.04            | 3.46            | 0.5 M NaClO₄ | 25 °C | 6    |
| L-Tartaric acid   | 3O          |                 |                 | $\beta_2=11.70$ | 0.1 M KNO₃  | 25 °C | 3    |
|                   |             |                 |                 | $\beta_2=11.3$  | 0.1 M NaClO₄ | 20 °C | 7    |
| Aspartic acid     | N2O         | 10.47           | 8.65            | 3.67            | 0.1 M NaClO₄ | 25 °C | 8    |
| Iminodiacectic acid | N2O    | 12.94           |                 |                 | 0.5 M NaClO₄ | 25 °C | 9    |
| HAD a             | N2O         | 12.50           |                 |                 | 0.1 M NaClO₄ | 20 °C | 10   |
| Diethylene triamine | 3N       | 17.4            |                 |                 | 0.5 M        | 25 °C | 11   |
| Glutamic acid     | N2O         | 10.47           | 8.28            | 3.50            | 0.1 M NaClO₄ | 20 °C | 10   |
| Picolinic acid    | NO          | 7.48            | 6.46            | 4.16            | 0.50 M NaNO₃ | 25 °C | 12   |
| Maltol            | 2O          | 11.90           | 8.98            | 8.69            | 0.50 M KNO₃  | 30 °C | 13   |
| Kojic acid        | 2O          | 10.78           | 8.56            | 7.51            | 0.50 M KNO₃  | 30 °C | 13   |
| 2-Picolyl amine   | 2N          | 9.6             |                 |                 | 0.5 M        | 25 °C | 11   |
| Ascorbic acid     | 3O          | 25.3            |                 |                 | 0.50 M NaNO₃ | 25 °C | 14   |
| Citric acid       | 4O          | 13.48           |                 |                 | 25 °C        | 11   |
|                   |             | 11.80           |                 |                 | 0.1 M KNO₃  | 25 °C | 5    |
|                   |             | 10.78           | 5.05            |                 | 0.15 M NaNO₃ | 37 °C | 15   |
| Nitrilotriacetic acid | N2O | 17.55           |                 |                 | 0.60 M NaClO₄ | 25 °C | 16   |
|                   |             | 18.2            |                 |                 | 0.10 M NaClO₄ | 25 °C | 17   |
|                   |             | 17.54           | 9.01            |                 | 1.00 M NaClO₄ | 25 °C | 18   |
| Triethanol amine  | N3O         | 9.2             |                 |                 | 0.50 M NaClO₄ | 25 °C | 2    |
| Phthalic acid     | 2O          |                 |                 | $\beta_2=11.70$ | 0.1 M KNO₃  | 25 °C | 3    |
12-Crown-4 \(^b\) & 4O & 16.1 & 0.50 M NaClO\(_4\) & 25 °C & 19 \\
Cyclen \(^c\) & 4N & 21.9 & 0.50 M NaClO\(_4\) & 25 °C & 20 \\
EDTA \(^d\) & 2N4O & 26.7 & 1.00 M NaClO\(_4\) & 20 °C & 21 \\
CDTA \(^e\) & 2N4O & 26.41 & 1.00 M NaClO\(_4\) & 25 °C & 16 \\
DTPA \(^f\) & 2N4O & 27.20 & 1.00 M NaClO\(_4\) & 25 °C & 22 \\

\(^a\) Hydrazine-iminodiacetic acid \\
\(^b\) 1,4,7,10-Tetraoxacyclododecane \\
\(^c\) 1,4,7,10-Tetrazacyclododecane \\
\(^d\) Ethylenetetraacetic acid \\
\(^e\) trans-1,2-diaminocyclohexanetetraacetic acid \\
\(^f\) Diethylenetriaminepentaacetic acid

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Table S3. Physicochemical characteristics of fulvic acid and soil sample.
Data of 1R105F was obtained from the IHSS (2021).

|                          | Fulvic acid (1R105F) | Mor          |
|--------------------------|----------------------|--------------|
| Water (%)                | 66                   |              |
| pH(H₂O)                  | 3.58                 |              |
| BaCl₂-Extractable cations (cmol(+)/kg⁻¹)* |          |              |
| Na⁺                     | 0.49                 |              |
| K⁺                      | 0.64                 |              |
| Ca²⁺                    | 10.4                 |              |
| Mg²⁺                    | 3.46                 |              |
| HNO₃-Extractable Fe and Al (mol kg⁻¹) |          |              |
| Fe³⁺                    | 0.0021               |              |
| Al³⁺                    | 0.017                |              |
| Elemental composition (wt %) |          |              |
| C                       | 52.31                | 49.8         |
| N                       | 0.68                 | 1.35         |
| S                       | 0.46                 | 0.11         |
| Carboxyl groups (meq (g C)⁻¹) | 11.16            |              |

*cmol charge per kg soil.

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IHSS (International humic substance society). [http://www.humicsubstances.org/](http://www.humicsubstances.org/) Downloaded August 11, 2021.
Table S4. Survey of reported crystal structures of bismuth(III) compounds with coordination numbers 3-9.

### Three-coordination, trigonal pyramid

| CSD code  | Mean d(Bi-O) | Reference and compound |
|-----------|--------------|------------------------|
| FAVHOA   | 2.025 Å      | Mansfeld, D.; Mehring, M.; Schurmann, M. *Angew. Chem., Int. Ed.* 2005, 44, 245. Bi(OC(CH$_3$)$_2$)(t-O$_2$C$_3$)$_3$ |
| JIYLUY   | 2.040 Å      | Massiani, M.-C.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; ; Daran, J.-C. *Polyhedron* 1991, 10, 437. Bi(OSi(C$_3$H$_7$)$_3$)$_3$3C$_6$H$_5$O |
| NAXZAO   | 2.042 Å      | S.Pääläsmää, S.; Mansfeld, D.; Schurmann, M.; Mehring, M. Z. *Anorg. Anorg. Chem.* 2005, 633, 2433. Bi(OC$i$-$C_3$H$_2$)$_3$ |
| HURSUK   | 2.056 Å      | Hatanpää, T.; Vehkamäki, M.; Ritala, M.; Leskelä, M. *Dalton Trans.* 2010, 39, 3219. Bi-t-O$_2$C$_3$H$_3$ |
| HURTAQ   | 2.056 Å      | Hatanpää, T.; Vehkamäki, M.; Ritala, M.; Leskelä, M. *Dalton Trans.* 2010, 39, 3219. Bi-t-O$_2$C$i$-$C_3$H$_2$H$_3$ |
| SAJSOM   | 2.056 Å      | Mansfeld, D.; Mehring, M.; Schurmann, M. Z. *Anorg. Anorg. Chem.* 2004, 630, 1795. Bi(OSi(C$_3$H$_7$)$_3$)(t-O$_2$C$_3$)$_3$ |
| HUTBII   | 2.065 Å      | Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayarathna, L. K.; Hanna, T. A. *Inorg. Chem.* 2009, 48, 11002. Bi(OC$i$-$C_3$H$_2$H$_3$)$_3$ |
| HUTBOO   | 2.065 Å      | Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayarathna, L. K.; Hanna, T. A. *Inorg. Chem.* 2009, 48, 11002. Bi(OC$i$-$C_3$H$_2$)$_3$ |
| IDANUW   | 2.074 Å      | Hanna, T. A.; Keitany, G.; Ibarra, C; Sommer, R. D.; Rheingold, A. L. *Polyhedron* 2001, 20, 2451. Bi(OC$i$-$C_3$H$_2$)$_3$ |
| HUTBAA   | 2.085 Å      | Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayarathna, L. K.; Hanna, T. A. *Inorg. Chem.* 2009, 48, 11002. Bi(OC$i$-$C_3$H$_2$H$_3$)$_3$ |
| BUNCUI   | 2.087 Å      | D.Mendoza-Espinosa, D.; Hanna, T. A. *Inorg. Chem.* 2009, 48, 10312. [C$_{60}$H$_{14}$Bi$_4$O$_4$] C$_3$H$_4$O |
| TOQDOT   | 2.089 Å      | Liu, L.; Zakharov, L. N.; Golen, J. A.; Rheingold, A. L.; Hanna, T. A. *Inorg. Chem.* 2008, 47, 11143. [C$_{60}$H$_{14}$Bi$_4$O$_4$] |
| KAXYUD   | 2.091 Å      | Evans, W. J.; Hain Jr., J. H.; Ziller, J. W. *Chem. Commun.* 1989, 1628. Bi(OC$i$-$C_3$H$_2$H$_3$)$_3$ |
| BUNCIX   | 2.097 Å      | D.Mendoza-Espinosa, D.; Hanna, T. A. *Inorg. Chem.* 2009, 48, 10312. [C$_{60}$H$_{14}$Bi$_4$O$_4$] 2C$_3$H$_4$O |
| HUTCEF   | 2.098 Å      | Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayarathna, L. K.; Hanna, T. A. *Inorg. Chem.* 2009, 48, 11002. Bi(OC$i$-$C_3$H$_2$)$_3$ |
| LIRMUV01 | 2.105 Å      | Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayarathna, L. K.; Hanna, T. A. *Inorg. Chem.* 2009, 48, 11002. Bi(OC$i$-$C_3$H$_2$)$_3$ |
| LIRMUV   | 2.121 Å      | Brym, M.; Jones, C.; Junk, P. C. *Main Group Chem.* 2006, 5, 13. Bi(OC$i$-$C_3$H$_2$H$_3$)$_3$ |

**Mean:** 2.074 Å/17 structures

### Four-coordination, 3+1

| CSD code  | Mean d(Bi-O) | Reference and compound |
|-----------|--------------|------------------------|
| CEMBAY    | 2.121 + 2.729 Å | Andrews, P. C.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Kumar, I.; Maguire, M. *Angew. Chem., Int. Ed.* 2006, 45, 5638. [C$_{108}$H$_{146}$Bi$_{14}$O$_{26}$]·18(CH$_3$)$_2$CO |
| HAWHAQ    | 2.134 + 2.758 Å | Zan-Jiao Wang, Z.-J.; Zhang, L.-C.; Zhu, Z.-M.; Chen, W.-L.; You, W.-S.; Wang, E.-B. *Inorg. Chem. Commun.* 2012, 17, 151. Na$_4$K$_5$[Bi$_2$Co$_2$Sn$_2$W$_6$($C_3$H$_5$O$_3$)$_3$]25H$_2$O |
| HAWHEU    | 2.133 + 2.740 Å | Zan-Jiao Wang, Z.-J.; Zhang, L.-C.; Zhu, Z.-M.; Chen, W.-L.; You, W.-S.; Wang, E.-B. *Inorg. Chem. Commun.* 2012, 17, 151. K$_{10}$[Bi$_2$Mn$_2$Sn$_2$W$_6$($C_3$H$_5$O$_3$)$_3$]30H$_2$O |
| HOBMOD    | 2.118 + 2.678 Å | Rheingold, A. L.; Hanna, T. A. CCDC code 1905550, 2019. [C$_{98}$H$_{13}$Bi$_2$O$_5$] |

S10
HURTEU 2.146 + 2.389 Å  Hätänpää, T.; Vehkamäki, M.; Ritala, M.; Leskelä, M. Dalton Trans. 2010, 3219. [C$_{46}$H$_{56}$Bi$_2$O$_6$]

HUTCAB 2.132 + 2.479 Å Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayaratha, L. K.; Hanna, T. A. Inorg. Chem. 2009, 48, 11002. [C$_{21}$H$_{26}$Bi$_2$O$_6$]

HUTCJ 2.153 + 2.333 Å Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayaratha, L. K.; Hanna, T. A. Inorg. Chem. 2009, 48, 11002. [C$_{26}$H$_{50}$Bi$_2$O$_6$]

HUTCOP 2.139 + 2.609 Å Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayaratha, L. K.; Hanna, T. A. Inorg. Chem. 2009, 48, 11002. [C$_{49}$H$_{50}$Bi$_2$Li$_2$O$_6$]

HUSZUR 2.123 + 2.425 Å Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayaratha, L. K.; Hanna, T. A. Inorg. Chem. 2009, 48, 11002. [C$_{46}$H$_{50}$Bi$_2$O$_6$]

JAYVAJ 2.098 + 2.885 Å Preda, A. M.; Schneider, W. B.; Rainer, M.; Ruffer, T.; Schaarschmidt, D.; Lang, H.; Mehring, M. Dalton Trans. 2017, 46, 8269. [C$_{42}$H$_{54}$Bi$_2$O$_6$S$_6$]

LUPIQ 2.175 + 2.413 Å Mendoza-Espinosa, D.; Hanna, T. A. Inorg. Chem. 2009, 48, 7452. [C$_{118}$H$_{132}$Bi$_2$Mo$_6$O$_{22}$] 3C$_6$H$_8$OH

PEWKUY 2.137 + 2.791 Å Nehefe, U.N.; Roesky, H. W.; Jancik, V.; Pal, A.; Magull, J. Inorg. Chim. Acta 2007, 360, 1248. [C$_{12}$H$_{272}$Bi$_2$Cl$_2$N$_2$O$_{30}$] 2C$_6$H$_8$O.

PUKIA 2.143 + 2.485 Å Parola, S.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Bois, C. J. Chem. Soc., Dalton Trans. 1998, 737. [C$_{16}$H$_{13}$Ba$_4$Bi$_2$O$_8$]

QAWMIM 2.105 + 2.661 Å Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayaratha, L. K.; Hanna, T. A. Inorg. Chem. 2009, 48, 11002. [Bi$_2$C$_{46}$H$_{10}$O$_{12}$]

RADHEJ 2.131 + 2.493 Å James, S. C.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Weckenmann, U. J. Chem. Soc., Dalton Trans. 1996, 4159. [C$_{7}$H$_{13}$Bi$_3$C$_7$O$_8$] 3C$_6$H$_8$ClO.

RUMLER 2.109 + 2.770 Å Mendoza-Espinosa, D.; Hanna, T. A. Dalton Trans. 2009, 5211. [Bi$_2$C$_{15}$H$_{14}$O$_{16}$]

RUPKIX 2.131 + 2.529 Å Mendoza-Espinosa, D.; Rheingold, A. L.; Hanna, T. A. Dalton Trans. 2009, 5226. [Bi$_2$C$_{12}$H$_{16}$O$_{12}$] 2(C$_4$H$_6$)O.

RUPKOD 2.140 + 2.428 Å Mendoza-Espinosa, D.; Rheingold, A. L.; Hanna, T. A. Dalton Trans. 2009, 5226. [Bi$_2$C$_{46}$H$_{50}$O$_{12}$] 7C$_6$H$_8$O 2H$_2$O

SUCKOT 2.121 + 2.554 Å Roschke, F.; Thiele, G.; Dhenen, S.; Mehring, M. Main Group Met. Chem. 2019, 47, 46. [C$_{7}$H$_{14}$Bi$_2$O$_6$]

TAPNIJ 2.131 + 2.688 Å Mansfeld, D.; Miersch, L.; Ruffer, T.; Schaarschmidt, D.; Lang, H.; Bohle, T.; Troff, R. W.; Schalley, C. A.; Müller, J.; Mehring, M. Chem. Eur. J. 2011, 17, 14805. [Bi$_{13}$C$_{16}$H$_{25}$O$_{20}$] (C$_6$H$_8$O)$_2$ 19(C$_2$H$_2$)CO.

TAPNOP 2.134 + 2.601 Å Mansfeld, D.; Miersch, L.; Ruffer, T.; Schaarschmidt, D.; Lang, H.; Bohle, T.; Troff, R. W.; Schalley, C. A.; Müller, J.; Mehring, M. Chem. Eur. J. 2011, 17, 14805. [Bi$_{13}$C$_{12}$H$_{25}$O$_{11}$S$_6$] (C$_6$H$_8$O)$_3$ (OH)$_2$ 9.5 (C$_2$H$_2$)OS) H$_2$O Rheingold, A. L.; Hanna, T. A. CCDC code 1961497 [C$_{80}$H$_{117}$Bi$_2$Br$_2$O$_4$] [C$_{46}$H$_{50}$Bi$_2$BrO$_4$] 2C$_6$H$_8$O$_2$

TULBUY 2.182 + 2.411 Å Andrews, P.C.; Deacon, G. B.; Junk, P. C.; Kumar, I.; MacLellan, J. G. Organometallics 2009, 28, 3999. [C$_{10}$H$_{20}$Bi$_{10}$N$_{14}$O$_{36}$] 3.25C$_6$H$_8$OH 2H$_2$O

VEFPID 2.086 + 2.524 Å Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J. 2006, 12, 1767. [C$_{37}$H$_{52}$Bi$_3$O$_{25}$S$_{12}$] 3C$_6$H$_8$.

VEFPUS 2.079 + 2.500 Å Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J. 2006, 12, 1767. [C$_{42}$H$_{54}$Bi$_3$O$_{25}$S$_{12}$] 3C$_6$H$_8$.

VEFIQH 2.110 + 2.343 Å Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J. 2006, 12, 1767. [C$_{46}$H$_{50}$Na$_{10}$O$_{20}$S$_{12}$] 2C$_6$H$_8$.

XUTDOH 2.125 + 2.920 Å Chai, D.-F.; Ma, Z.; Yan, H.; Qiu, Y.; Liu, H.; Guo, H.-D.; Gao, G.-G. RSC Adv. 2015, 5, 78771. Na[C$_{42}$H$_{54}$Bi$_3$Cu$_2$N$_{28}$Na$_9$O$_{15}$W$_{14}$] 22H$_2$O

Mean: 2.127 + 2.591 Å/27 structures (mean of means: 2.243 Å)
Four-coordination, 2+2

| CSD code | Mean d(Bi-O) Å | Reference and compound |
|----------|----------------|-----------------------|
| BADNOL   | 2.104 + 2.332 Å | Rogow, D. L.; Fei, H.; Brennan, D. P.; Ikehata, M.; Zavalij, P. Y.; Oliver, A. G.; Oliver, S. J. Inorg. Chem. 2010, 49, 5619. [Bi2O4(OH)4][CF3SO4]4 |
| BADNUR   | 2.126 + 2.376 Å | Rogow, D. L.; Fei, H.; Brennan, D. P.; Ikehata, M.; Zavalij, P. Y.; Oliver, A. G.; Oliver, S. J. Inorg. Chem. 2010, 49, 5619. [Bi2(OH)4][CF3SO4]4 |
| CECWAJ   | 2.122 + 2.334 Å | Mehring, M.; Paalasmaa, S.; Schurmann, M. Eur. J. Inorg. Chem. 2005, 4891. [C8H18Bi2Na2O5Si12]3C3H6 |
| CECWEN   | 2.081 + 2.322 Å | Mehring, M.; Paalasmaa, S.; Schurmann, M. Eur. J. Inorg. Chem. 2005, 4891. [C8H18Bi2Na2O5Si12]3C3H6 |
| CECWIR   | 2.051 + 2.307 Å | Mehring, M.; Paalasmaa, S.; Schurmann, M. Eur. J. Inorg. Chem. 2005, 4891. [C8H18Bi2Na2O5Si12]3C3H6 |
| ERUBAW   | 2.100 + 2.333 Å | D. Mendoza-Espinosa, D. Dalton Trans. 2016, 45, 13399. [C26H23Bi2O12]3C3H6O |
| FAVHUG   | 2.106 + 2.281 Å | Mansfeld, D.; Mehring, M.; Schurmann, M. Angew. Chem., Int. Ed. 2005, 44, 245. [C8H18Bi2O4Si12]2C3H6 |
| FEVNUQ   | 2.160 + 2.444 Å | Geisselmann, A.; Klufers, P.; Kropfgans, C.; Mayer, P.; Piotrowski H. Angew. Chem. Int. Ed. 2005, 44, 924. Na4[C22H80Bi4O60]53H2O |
| JAXBAM   | 2.081 + 2.306 Å | Thurston, J. H.; Swenson, D. C.; Messerle, L. Chem. Commun. 2005, 4228. [C8H18Bi4O12][ClO4]4·C3H4OH |
| MIZQUI   | 2.131 + 2.337 Å | Andrews, P. C.; Junk, P. C.; Nuzhnaya, I.; Spiccia, L. Dalton Trans. 2008, 2557. [C8H18BiFe2O2] |
| MIZRAP   | 2.074 + 2.306 Å | Andrews, P. C.; Junk, P. C.; Nuzhnaya, I.; Spiccia, L. Dalton Trans. 2008, 2557. [C8H18BiFe2O2] |
| NOFPUT   | 2.172 + 2.250 Å | Klufers, P.; Mayer, P. Acta Crystallogr., Sect. C 1998, 54, 583. Na0.5[(C24H48Bi6O26)(OH)]·3H2O Bi·Bi = 3.97 Å |
| PAWZIW   | 2.079 + 2.354 Å | Parola, S.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Jagner, S.; Håkansson, M. J. Chem. Soc., Dalton Trans. 1997, 4631. [C8H3Bi3O12][Ti3] |
| RUPLEU   | 2.188 + 2.239 Å | Mendoza-Espinosa, D.; Reginold, A. L.; Hanna, T. A. Dalton Trans. 2009, 5226. [Bi13C15H30O16][5.5C3H6O2·2C3H14 |
| SICHAO   | 2.123 + 2.200 Å | Klufers, P.; Mayer, P. Z. Anorg. Allg. Chem. 2007, 633, 903. [Co(NH3)6][(C24H32Bi16O40)]·9H2O |
| SICHIW   | 2.160 + 2.246 Å | Klufers, P.; Mayer, P. Z. Anorg. Allg. Chem. 2007, 633, 903. [Na2[(C24H48Bi6O26)(OH)]·3H2O Bi·Bi = 3.97 Å |
| VEDGOB   | 2.127 + 2.242 Å | Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J. 2006, 12, 1767. [C8H18Bi3Na4O3Si18] |
| VEFQON   | 2.063 + 2.258 Å | Mehring, M.; Mansfeld, D.; Costisella, B.; Schurmann, M. Eur. J. Inorg. Chem. 2006, 735. [C8H18Bi3Li12O12Si2]·2C3H6CH3 |
| VEGPON   | 2.063 + 2.258 Å | Mehring, M.; Mansfeld, D.; Costisella, B.; Schurmann, M. Eur. J. Inorg. Chem. 2006, 735. [C8H18Bi3Li12O12Si2]·1.5C3H6 |
| YEGDIZ   | 2.162 + 2.396 Å | Miersch, L.; Ruffer, T.; Schlesinger, M.; Lang, H.; Mehring, M. Inorg. Chem. 2012, 51, 9376. [Bi2O4(OH)4](NO3)4·H2O |
| YEGDUL   | 2.160 + 2.371 Å | Miersch, L.; Ruffer, T.; Schlesinger, M.; Lang, H.; Mehring, M. Inorg. Chem. 2012, 51, 9376. [Bi2O4(OH)4](NO3)4·3H2O |
| ZAVMUE   | 2.068 + 2.276 Å | Veith, M.; Yu, E.-C.; Huch, V. Chem. Eur. J. 1995, 1, 26. [C32H23Bi2K4O8] |

Mean: 2.115 + 2.299 Å/22 structures (mean of means: 2.207 Å)

Five-coordination

| CSD code | Reference, bond distances, geometry and compound |
|----------|--------------------------------------------------|
| CECWAJ   | Mehring, M.; Paalasmaa, S.; Schurmann, M. Eur. J. Inorg. Chem. 2005, 4891. 2.099, 2.212, 2.303, 2.315, 2.578/2.666, 2.255, 2.310, 2.312, 2.531, mean 2.298 Å - distorted square pyramid, [C8H18Bi3Na2O5Si12]3C3H6 |
| CECWEN   | Mehring, M.; Paalasmaa, S.; Schurmann, M. Eur. J. Inorg. Chem. 2005, 4891. 2.083, 2.173, 2.190, 2.503, 2.704/2.884, 2.219, 2.278, 2.333, 2.346, mean 2.291 Å - distorted square pyramid, [C8H18Bi3Na2O5Si12]3C3H6 |
| CEMBAY   | Andrews, P. C.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Kumar, I.; Maguire, M. Angew. Chem., Int. Ed. 2006, 45, 5638. 2.083, 2.120, 2.151, 2.762, 2.800, mean 2.383 Å; [C18H146Bi3O126]18(CH3)2CO |

S12
DOLDAJ Whitmire, K. H.; Hoppe, S.; Sydora, O.; Jolas, J. L.; Jones, C. M. Inorg. Chem. 2000, 39, 85. 2.108, 2.131, 2.266, 2.387, 2.628, mean 2.304 Å - distorted square pyramid, [CsH_{16}BiF_{6}O_{4}]_n·C_{6}H_{6}.

DOLDEN Whitmire, K. H.; Hoppe, S.; Sydora, O.; Jolas, J. L.; Jones, C. M. Inorg. Chem. 2000, 39, 85. 2.108, 2.220, 2.311, 2.356, 2.433, mean 2.286 Å - distorted square pyramid, [Cs_{6}BiF_{6}O_{4}]_3·3.37CH_{2}Cl_{2}.

DOLDUD Whitmire, K. H.; Hoppe, S.; Sydora, O.; Jolas, J. L.; Jones, C. M. Inorg. Chem. 2000, 39, 85. 2.042, 2.187, 2.290, 2.338, 2.532, mean 2.278 Å - distorted square pyramid, [Cs_{6}H_{16}BiF_{6}O_{4}]_1.

DOLUJ Whitmire, K. H.; Hoppe, S.; Sydora, O.; Jolas, J. L.; Jones, C. M. Inorg. Chem. 2000, 39, 85. 2.154, 2.187, 2.285, 2.331, 2.467, mean 2.285 Å - distorted square pyramid, [Cs_{6}H_{16}BiF_{6}O_{4}]_1.

EBIHED Lihua Liu; Zakharov, L. N.; Rheingold, A. L.; Hanna, T. A. Chem. Commun. 2004, 1472. 2.161, 2.169, 2.173, 2.420, 2.421/2.236, 2.244, 2.254, 2.258, 2.475 Å, mean 2.258 Å - distorted square pyramid, [C_{17}H_{29}Bi_{2}O_{10}]_{2}·C_{6}H_{6}.

ECOKUC Mehring, M.; Schurmann, M. Chem. Commun. 2001, 2354. 2.120, 2.212, 2.212, 2.438, 2.438 Å, mean 2.284 Å - distorted square pyramid, [Cs_{6}H_{16}Bi_{4}O_{6}P_{12}]·3C_{6}H_{6}·H_{2}O.

EYOSEQ Sharutin, V. V.; Egorova, I. V.; Sharutina, O. K.; Ivanenko, T. K.; Adonin, N. Y.; Starichenko, V. F.; Pushilin, M. A.; Gerasimenko, A. V. Koord. Khim. 2003, 29, 902. 2.119, 2.276, 2.308, 2.384, 2.387 Å, mean 2.295 Å, Bi···Bi = 3.806 Å - distorted square pyramid, [Cs_{6}H_{16}Bi_{2}F_{2}O_{18}]_{2}·C_{6}H_{6}.

FAQNAN Thruston, J. H.; Kumar, A.; Hofmann, C.; Whitmire, K. H. Inorg. Chem. 2004, 43, 8427. 2.127, 2.194, 2.320, 2.328, 2.517/2.186, 2.273, 2.366, 2.289, 2.606 Å, mean 2.321 Å, Bi···Bi = 4.347 Å - distorted square pyramid, [Cs_{6}H_{16}Bi_{2}Ti_{2}O_{18}]_{2}·C_{6}H_{6}.

FASYII Thruston, J. H.; Kumar, A.; Hofmann, C.; Whitmire, K. H. Inorg. Chem. 2004, 43, 8427. 2.104, 2.276, 2.299, 2.368, 2.454, mean 2.300 Å - distorted square pyramid, [Cs_{18}H_{29}Bi_{4}Ti_{4}O_{16}]·C_{6}H_{6}.

FAVHUG Mansfeld, D.; Mehring, M.; Schurmann, M. Angew. Chem., Int. Ed. 2005, 44, 245. 2.113, 2.269, 2.286, 2.339, 2.470/2.112, 2.128, 2.134, 2.528, 2.562 Å, mean 2.294 Å - distorted square pyramid, [Cs_{6}H_{16}Bi_{2}O_{4}Si_{14}]·2C_{6}H_{6}.

JAXBAM Thruston, J. H.; Swenson, D. C.; Messerle, L. Chem. Commun. 2005, 4228. 2.178, 2.184, 2.225, 2.511, 2.687/2.177, 2.182, 2.205, 2.499, 2.605 Å, mean 2.345 Å - distorted square pyramid, [Cs_{20}H_{32}Bi_{2}O_{14}]·(ClO_{3})_{2}·4C_{2}H_{5}OH.

JUMZIA Jones, C. N.; Burkart, M. D.; Whitmire, K. H. Chem. Commun. 1992, 1638. 2.119, 2.211, 2.301, 2.349, 2.411 Å, mean 2.278 Å, Bi···Bi = 4.002 Å - distorted square pyramid, [Cs_{6}H_{16}Bi_{4}O_{6}S_{2}]·C_{6}H_{6}O.

JUMZOG Jones, C. N.; Burkart, M. D.; Whitmire, K. H. Chem. Commun. 1992, 1638. 2.105, 2.139, 2.262, 2.565, 2.632/2.189, 2.233, 2.239, 2.457, 2.619 Å, mean 2.344 Å - distorted square pyramid, [Cs_{26}Bi_{2}F_{6}O_{20}]·2C_{2}H_{6}.

JUMZOG01 Whitmire, K. H.; Hoppe, S.; Sydora, O.; Jolas, J. L.; Jones, C. M. Inorg. Chem. 2000, 39, 85. 2.116, 2.120, 2.217, 2.511, 2.537/2.179, 2.229, 2.230, 2.450, 2.610 Å, mean 2.320 Å - distorted square pyramid, [Bi_{2}H_{2}O_{4}][F_{2}(NO_{3})_{2}].

NEMMOI 2.164, 2.296, 2.322, 2.556, 2.593 Å, mean 2.386 Å - distorted square pyramid, [Cs_{20}Bi_{2}F_{6}O_{20}]·2C_{2}H_{6}.

PEWKUY Nehete, U.N.; Roehsy, H. W.; Jancik, V.; Pal, A.; Magull, J. Inorg. Chim. Acta 2007, 360, 1248/2.086, 2.155, 2.307, 2.510, 2.672 Å, mean 2.346 Å - distorted square pyramid, [Cs_{15}H_{2}O_{4}Bi_{2}Cl_{4}Na_{6}O_{6}Si_{16}]·2C_{6}H_{6}.

RADHEJ James, S. C.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Weckemann, U. J. Chem. Soc., Dalton Trans. 1996, 4159. 2.094, 2.252, 2.273, 2.335, 2.478/2.122, 2.147, 2.368, 2.399, 2.757 Å, mean 2.323 Å - distorted square pyramid, [Cs_{2}H_{3}Bi_{2}Cl_{3}O_{3}]·C_{6}H_{6}O·C_{6}H_{5}Cl_{2}O.

SELFEU01 Matchett, M. A.; Ciang, M. Y.; Buhro, W. E. Inorg. Chem. 1999, 29, 358. 2.108, 2.203, 2.209, 2.528, 2.578/2.072, 2.205, 2.2112.542, 2.562 Å, mean 2.322 Å, Bi···Bi = 3.953 Å - distorted square pyramid, [Cs_{6}H_{16}Bi_{2}Cl_{2}]_{6}.

VEFPIC Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J. 2006, 12, 1767. 2.065, 2.196, 2.260, 2.313, 2.407 Å, mean 2.248 Å - distorted square pyramid, [Cs_{2}H_{3}Bi_{2}O_{6}Si_{2}]·3C_{6}H_{6}.

VEFPOM Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J. 2006, 12, 1767.
Inorg. Chem. Commun. 2002, 549.

XONGOW Thurston, J. H.; Whitmire, K. H. Inorg. Chem. 2002, 5, 549. 2.050, 2.096, 2.147, 2.631, 2.658/2.081, 2.088, 2.129, 2.476, 2.618, mean 2.297 Å, Bi···Bi = 3.942 Å - distorted square pyramid, [C$_8$H$_{120}$Bi$_3$O$_{25}$]·6C$_2$H$_5$OH.

Mean: 2.301 Å/33 structures

Six-coordination – distorted octahedron

CSD code Mean (d(Bi-O)) Reference and compound
CECWEN 2.155 + 2.641 Å Mehring, M.; Paalasmaa, S.; Schurmann, M. Eur. J. Inorg. Chem. 2005, 4891. [C$_{48}$H$_{114}$Bi$_3$Na$_2$O$_{25}$Si$_{12}$]·1.5C$_2$H$_5$
CEMBAY 2.314 + 2.558 Å Andrews, P. C.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Kumar, I.; Maguire, M. Angew. Chem., Int. Ed. 2006, 45, 5638. [C$_{18}$H$_{16}$Bi$_3$O$_{25}$]18(CH$_3_2$)CO
DOLDAJ 2.218 + 2.494 Å Whitmire, K. H.; Hoppe, S.; Sudora, O.; Jolas, J. L.; Jones, C. M. Inorg. Chem. 2000, 39, 85. [C$_{68}$H$_{134}$Bi$_3$F$_6$O$_{16}$]·3C$_2$H$_5$
ICOVUR 2.081 + 2.831 Å Williams, P. A.; Jones, A. C.; Crosbie, M. J.; Wright, P. J.; Bickley, J. F.; Steiner, A.; Davies, H. O.; Leedham, T. J.; Critchlow, G. W. Chem. Vap. Deposition 2001, 7, 205. [Bi$_2$(C$_3$H$_{11_2}$)$_3$]
JAXBAM 2.181 + 2.614 Å Thurston, J. H.; Swenson, D. C.; Messerle, L. Chem. Commun. 2005, 4228. [C$_{20}$H$_{30}$Bi$_3$O$_{13}$][ClO$_4$]·4C$_2$H$_5$OH.
JUJVF 2.320 + 2.561 Å Troyanov, S. I.; Pisarevskii, A. P. Koord. Khim. 1991, 17, 909. [Bi(O$_2$CH$_3$)$_3$]
JUMZIA 2.249 + 2.556 Å Jones, C. N.; Burkart, M. D.; Whitmire, K. H. Chem. Commun. 1992, 1638. [C$_{62}$H$_{10}$Bi$_6$F$_6$O$_{16}$]·C$_4$H$_8$O
NAXZES 2.064 + 3.121 Å Paalasmaa, S.; Mansfeld, D.; Schurmann, M.; Mehring, M. Z. Anorg. Allg. Chem. 2005, 651, 2433. [C$_2$H$_5$Bi$_3$O$_{13}$]
NOFPUS 2.166 + 2.665 Å Klufers, P.; Mayer, P. Acta Crystallogr., Sect. C 1998, 54, 583. Na$_{12}$([C$_4$H$_{10}$Bi$_3$O$_{12}$][OH])$_3$·3H$_2$O.
VEFPIG 2.178 + 2.669 Å Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J. 2006, 12, 1767. [C$_2$H$_{32}$Bi$_3$O$_{25}$Si$_{12}$]3C$_2$H$_5$.
VEFPOM 2.218 + 2.588 Å  
Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J.  
2006, 12, 1767. [C_{37}H_{21}Bi_2O_{36}Si_{22}]: 3C-H_3

VEFQAZ 2.177 + 2.698 Å  
Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J.  
2006, 12, 1767. [C_{37}H_{17}Bi_2O_{36}Si_{17}]: 0.5C-H_6

VEFQIH 2.171 + 2.531 Å  
Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J.  
2006, 12, 1767. [C_{37}H_{32}Bi_2O_{36}Si_{22}]: 2C-H_6

VEFQON 2.171 + 2.747 Å  
Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J.  
2006, 12, 1767. [C_{37}H_{12}Bi_2O_{36}Si_{18}]:

WAYYEA 2.153 + 2.652 Å  
Jones, C. M.; Burkart, M. D.; Bachman, R. E.; Serra, D. L.; Shiu-Jyh Hwu;  
Whitmire K. H. Inorg. Chem. 1993, 32, 5136. [C_{37}H_{32}Bi_2F_{36}O_{10}]: C_6H_{13}

WAYYEA 2.169 + 2.613 Å  
Jones, C. M.; Burkart, M. D.; Bachman, R. E.; Serra, D. L.; Shiu-Jyh Hwu;  
Whitmire K. H. Inorg. Chem. 1993, 32, 5136. [C_{37}H_{32}Bi_2F_{36}O_{10}]:

XONGEM 2.253 + 2.594 Å  
Thurston, J. H.; Whitmire, K. H. Inorg. Chem. 2002, 41, 4194.  
[C_{68}H_{36}Bi_2Nb_3O_{23}]

XONGIQ 2.268 + 2.606 Å  
Thurston, J. H.; Whitmire, K. H. Inorg. Chem. 2002, 41, 4194.  
[C_{68}H_{36}Bi_2Cl_{3}O_{23}]:

XONGOW 2.252 + 2.552 Å  
Thurston, J. H.; Whitmire, K. H. Inorg. Chem. 2002, 41, 4194.  
[C_{68}H_{36}Bi_2O_{23}]:

XOVPED 2.129 + 2.662 Å  
Kessler, V. G.; Turova, N. Y.; Turevskaya, E. P.  
Inorg. Chem. Commun. 2002, 5, 549. [C_{30}H_{25}Bi_6O_{25}]: 2C-H_3OH.

Mean: 2.194 + 2.648 Å/20 structures

VEGDUB 2.390 Å  
Mehring, M.; Mansfeld, D.; Costisella, B.; Schurmann, M. Eur. J. Inorg. Chem. 2006, 735.  
[C_{37}H_{48}Bi_3Li_3O_{13}Si_{18}]: 2C-H_3

VEFPUS 2.392 Å  
Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. Chem. Eur. J.  
2006, 12, 1767. [C_{37}H_{48}Bi_3O_{36}Si_{18}]: 2C-H_3

VEGQON 2.393 Å  
Mehring, M.; Mansfeld, D.; Costisella, B.; Schurmann, M. Eur. J. Inorg. Chem. 2006, 735.  
[C_{38}H_{48}Bi_3Li_3O_{13}Si_{18}]: 1.5C-H_3.

Mean: 2.417 Å/23 structures

Six-coordination – regular octahedron

CSD code | Mean d(Bi-O) | Reference and compound
---|---|---
TESYUL | 2.324 Å | García-Montalvo, V.; Cea-Olivares, R.; Williams, D. J.; Espinosa-Perez, G. Inorg. Chem. 1996, 35, 3948. almost regular octahedron. [Bi(O_2P_2N(C_2H_2))_2].
WOPVIG | 2.323 Å | Näslund, J.; Persson, I.; Sandström, M. Inorg. Chem. 2000, 39, 4012. almost regular octahedron. [Bi(OCN(CH_2)_3(CH_3)_2)_3][OC(OH)]_3.
YOGPAL | 2.311 Å | Carmalt, C. J.; Farrugia, L. J.; Norman, N. C. Z. Anorg. Allg. Chem. 1995, 621, 47. regular octahedron. [Bi(OCN(CH_2)_3(CH_3)_2)_3]Bi_4I_2.

Mean: 2.319 Å/3 structures

Six-coordination – distorted pentagonal pyramid

CSD code | Mean d(Bi-O) | Reference and compound
---|---|---
DOLDEN | 2.367 Å | Whitmire, K. H.; Hoppe, S.; Sydora, O.; Jolas, J. L.; Jones, C. M. Inorg. Chem. 2000, 39, 85. [C_{36}Bi_2F_{36}O_{26}]: 3.57CH_2Cl.
EYSEQ | 2.392 Å | Sharutina, V. V.; Egorova, I. V.; Sharutina, O. K.; Ivanenko, T. K.; Adonin, N. Y.; Starichenko, V. F.; Pushlin, M. A.; Gerasimenko, A. V. Koord. Khim. 2003, 29, 902. [C_{36}H_{16}Bi_2F_{32}O_{18}]: 2C-H_8
HARGUC | 2.389 Å | Asato, E.; Katsura, K.; Mikuriya, M.; Fujii, T.; Reedijk, J. Inorg. Chem. 1993, 32, 5322. (H,N)[C_2H_2Bi_2O_{15}]: 2H_2O
HEMIZQ | 2.347 Å | Arnelo, L.; Bandoli, G.; Casarin, M.; Depaoli, G.; Tondello, A.; E. Vittadini, A. Inorg. Chim Acta 1998, 275, 340. [Bi_2(O_2C_2H_4)_3]: H_2O
HEMQOF | 2.335 Å | Arnelo, L.; Bandoli, G.; Casarin, M.; Depaoli, G.; Tondello, A.; E. Vittadini, A. Inorg. Chim Acta 1998, 275, 340. [Bi_2(O_2C_2H_4)_3]: 3H_2O
JIRYUE | 2.378 Å | Herrmann, W. A.; Herdtweck, E.; Pajdlam L. Inorg. Chem. 1991, 30, 2579. K_2[Bi_2C_2H_{10}O_{15}]: 3H_2O
JUMZOG 2.381 Å
JUMZOG01 2.381 Å

Whitmire, K. H.; Hoppe, S.; Sydora, O.; Jolas, J. L.; Jones, C. M. Inorg. Chem. 2000, 39, 85. [C₇₈Bi₁₂F₆₅O₂₅] 2C₄H₆

MUZVEI 2.465 Å
MUZVIM 2.453 Å

Thurston, J. H.; Whitmire, K. H. Inorg. Chem. 2003, 42, 201. [C₆₀H₉₀Bi₁₂O₂₅]

NAPBOW 2.350 Å

Dikarev, E. V.; Haitao Zhang; Bo Li J. Am. Chem. Soc. 2005, 127, 6156. [C₆₀H₁₂Bi₁₂F₆₅MnO₁₅]

NAPBUC 2.348 Å

Dikarev, E. V.; Haitao Zhang; Bo Li J. Am. Chem. Soc. 2005, 127, 6156. [C₆₀H₁₂Bi₁₂F₆₅FeO₁₅]

NAPCAJ 2.351 Å

Dikarev, E. V.; Haitao Zhang; Bo Li J. Am. Chem. Soc. 2005, 127, 6156. [C₆₀H₁₂Bi₁₂F₆₅CoO₁₅]

NAPCEN 2.353 Å

Dikarev, E. V.; Haitao Zhang; Bo Li J. Am. Chem. Soc. 2005, 127, 6156. [C₆₀H₁₂Bi₁₂F₆₅NiO₁₅]

NAPCIR 2.342 Å

Dikarev, E. V.; Haitao Zhang; Bo Li J. Am. Chem. Soc. 2005, 127, 6156. [C₆₀H₁₂Bi₁₂F₆₅CuO₁₅]

NAPCOX 2.350 Å

Dikarev, E. V.; Haitao Zhang; Bo Li J. Am. Chem. Soc. 2005, 127, 6156. [C₆₀H₁₂Bi₁₂F₆₅ZnO₁₅]

NAPCUD 2.345 Å

Dikarev, E. V.; Haitao Zhang; Bo Li J. Am. Chem. Soc. 2005, 127, 6156. [BiO(C₆H₅)₂][Bi(O₂C)₆]

WIJYIX 2.336 Å

Jones, C. M.; Burkart, M. D.; Bachman, R. E.; Serra, D. L.; Shiou-Jyh Hwu; Whitmire K. H. Inorg. Chem. 1993, 32, 5136. [BiO(C₂H₅)₂]

XATWOF 2.379 Å

Sharutina, V.V.; Sharutina, I.V.; Egorova, O.K.; Sharutina, T.K.; Ivanenko, N.Yu.; Adonin, A.V.; Starichenko, V.F.; Egorova, I.V.; Sharutina, O.K.; Ivanenko, T.K.; Adonin, N.Y.; Starichenko, V.F.; Pushilin, M.A.; Gerasimenko, A.V. Koord. Khim. 2005, 31, 4. [C₅₆H₁₂Bi₁₂F₆₅O₁₅] 2C₄H₁₀

XATWUL 2.389 Å

Sharutin, V.V.; Sharutina, I.V.; Egorova, O.K.; Sharutina, T.K.; Ivanenko, N.Yu.; Adonin, A.V.; Starichenko, V.F.; Egorova, I.V.; Sharutina, O.K.; Ivanenko, T.K.; Adonin, N.Y.; Starichenko, V.F.; Pushilin, M.A.; Gerasimenko, A.V. Koord. Khim. 2005, 31, 4. [C₅₆H₁₂Bi₁₂F₆₅O₁₅] 4C₄H₁₀

YUBNIS 2.355 Å

Asato, E.; Katsura, K.; Mikuriya, M.; Turpeinen, U.; Mutikainen, I.; Reedijk, J. Inorg. Chem. 1995, 34, 2447. (NH₄)₁₂[C₆₀H₁₂Bi₁₂O₁₆]·10H₂O.

Mean: 2.361 Å/19 structures

Six-coordination with extreme gap

| CSD code | Mean d(Bi-O) | Reference and compound |
|----------|--------------|------------------------|
| SUFFAA   | 2.394 Å      | Troyanov, S. I.; Pisarevsky, A. P. Chem. Commun. 1993, 335. [C₆₀H₁₀₆Bi₁₂O₂₄] |

Seven-coordination

| CSD code | Reference, bond distances, geometry and compound |
|----------|--------------------------------------------------|
| ALOLES   | Wei Li; Lan Jin; Nianyong Zhu; Xuemei Hou; Feng Deng; Hongzhe Sun J. Am. Chem. Soc. 2003, 125, 12408. 2.101, 2.376, 2.381, 2.445, 2.453, 2.509, 2.790, mean 2.436 Å, Bi···Bi = 4.338 Å - distorted monocapped octahedron, (NH₄)₉K₁₁[C₆₀H₁₂Bi₁₂O₁₆]·14H₂O. |
| CEMBAY   | Andrews, P. C.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Kumar, I.; Maguire, M. Angew. Chem., Int. Ed. 2006, 45, 5638. 2.176, 2.204, 2.235, 2.545, 2.759, 2.784, 2.824 Å, mean 2.504 Å - distorted monocapped octahedron, [C₁₅₈H₁₄₈Bi₁₂O₁₂₆]·18(CH₃)₂CO. |
| CEMBEC   | Andrews, P. C.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Kumar, I.; Maguire, M. Angew. Chem., Int. Ed. 2006, 45, 5638. 2.132, 2.140, 2.313, 2.364, 2.681, 2.731, 2.951 Å, mean 2.473 Å - distorted monocapped octahedron, [C₁₅₈H₁₄₈Bi₁₂O₁₂₆]·1.5((CH₃)₂CO. |
| ECOKUC   | Mehring, M.; Schurrmann, M. Chem. Commun. 2001, 2354. 2.209, 2.230, 2.230, 2.554, 2.554, 2.664, 2.664, mean 2.444 Å - bicapped pentagon, [C₄₈H₁₁₆Bi₁₂O₁₆P₁₂·3C₆H₁₂O₆]. |
FAQMUG  Thurston, J. H.; Kumar, A.; Hofmann, C.; Whitmire, K. H. *Inorg. Chem.* 2004, 43, 8427.
2.277, 2.316, 2.326, 2.400, 2.534, 2.545, 2.691, mean 2.441 Å - bicapped pentagon,
[C$_{9}$H$_{18}$Bi$_{5}$Ti$_{3}$O$_{3}$].

FASYII  Thurston, J. H.; Kumar, A.; Hofmann, C.; Whitmire, K. H. *Inorg. Chem.* 2004, 43, 8427.
2.108, 2.356, 2.368, 2.378, 2.530, 2.645, 2.678, mean 2.438 Å - bicapped pentagon,
[C$_{18}$H$_{32}$Bi$_{5}$Ti$_{3}$O$_{14}$]

KOFDEO  Hunger, M.; Limberg, C.; Kircher, P. *Organometal.* 2000, 19, 1044.
2.181, 2.203, 2.226, 2.572, 2.594, 2.648, 2.708 Å, mean 2.447 Å - bicapped pentagon,
[C$_{9}$H$_{18}$Bi$_{5}$MoO$_{4}$].

MUMKEK  Andrews, P. C.; Deacon, G. B.; Jackson, W. R.; Maguire, M.; Scott, N. M.; Skelton, B. W.; White, A. H. J. Chem. Soc., Dalton Trans. 2002, 4634.
2.207, 2.236, 2.326, 2.496, 2.515, 2.532, 2.758 Å, mean 2.439 Å, Bi – Bi = 4.123 Å - distorted
monocapped octahedron, [C$_{3}$H$_{4}$Bi$_{2}$O$_{3}$].

MUZVAE  Thurston, J. H.; Whitmire, K. H. *Inorg. Chem.* 2003, 42, 142.
2.221, 2.275, 2.300, 2.489, 2.499, 2.639, 2.738, mean 2.452 Å – distorted monocapped
octahedron, [C$_{9}$H$_{18}$Bi$_{5}$Nb$_{2}$O$_{27}$]·3C$_{2}$H$_{6}$H$_{2}$O.

MUZTUW  Thurston, J. H.; Whitmire, K. H. *Inorg. Chem.* 2003, 42, 142.
2.222, 2.289, 2.306, 2.499, 2.499, 2.637, 2.750, mean 2.457 Å – distorted
monocapped octahedron, [C$_{3}$H$_{4}$Bi$_{2}$Ta$_{2}$O$_{27}$]·3C$_{2}$H$_{6}$H$_{2}$O.

TEVPUF  Feldmann, C. *Inorg. Chem.* 2001, 40, 818.
2.192, 2.257, 2.315, 2.552, 2.562, 2.614, 2.718, mean 2.459 Å – bicapped pentagon,
[C$_{3}$H$_{4}$Bi$_{3}$O$_{12}$][Bi$_{5}$Cu$_{11}$].

VEFPIG  Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. *Chem. Eur. J.* 2006, 12, 1767.
2.097, 2.247, 2.266, 2.371, 2.745, 2.991, 3.371, mean 2.584 Å – bicapped pentagon,
[C$_{9}$H$_{18}$Bi$_{5}$Ta$_{2}$O$_{27}$]·3C$_{2}$H$_{6}$.

VEQH  Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. *Chem. Eur. J.* 2006, 12, 1767.
2.136, 2.233, 2.252, 2.390, 2.569, 3.054, 3.406 Å, mean 2.577 Å, – bicapped pentagon,
[C$_{3}$H$_{4}$Bi$_{3}$Na$_{2}$O$_{9}$S$_{12}$]·2C$_{2}$H$_{6}$.

VEQON  Mehring, M.; Mansfeld, D.; Paalasmaa, S.; Schurmann, M. *Chem. Eur. J.* 2006, 12, 1767.
2.111, 2.281, 2.344, 2.421, 2.436, 2.991, 3.008 Å, mean 2.513 Å, – distorted octahedron,
[C$_{3}$H$_{4}$Bi$_{3}$Na$_{2}$O$_{9}$S$_{18}$]·H$_{2}$O.

XATWUL  Sharutin, V.V.Sharutin, I.V.Egorova, O.K.Sharutina, T.K.Ivanenko, N.Yu.Adonin,
V.F.Starichenko, M.A.Pushilin, A.V.Gerasimenko. V.; Egorova, I. V.; Sharutina, O. K.;
Ivanenko, T. K.; Adonin, N. Y.; Starichenko, V. F.; Pushilin, M. A.; Gerasimenko, A V.
*Koord. Khim.* 2005, 31, 4.
2.124, 2.276, 2.295, 2.391, 2.425, 2.833, 2.860 Å, mean 2.458 Å - bicapped pentagon,
[C$_{3}$H$_{4}$Bi$_{3}$F$_{3}$O$_{18}$]·4C$_{2}$H$_{10}$.

XONGUC  Thurston, J. H.; Whitmire, K. H. *Inorg. Chem.* 2002, 41, 4194.
2.237, 2.309, 2.320, 2.417, 2.476, 2.607, 2.622 Å, mean 2.427 Å - tricapped square,
[C$_{7}$H$_{14}$Bi$_{3}$Ti$_{3}$O$_{30}$]·2C$_{2}$H$_{4}$.

YIJYEV  Fukin, G. K.; Pisarevski, A. P.; Yanovsky, A. I.; Struchkov, Y. T. Zn. Neorg. Khim. 1993, 38, 1205.
2.133, 2.315, 2.344, 2.383, 2.384, 2.391, 3.073 Å, mean 2.432 Å - distorted monocapped
octahedron, [C$_{6}$H$_{10}$(CH$_{3}$)$_{3}$]·0.5(CH$_{3}$)$_{3}$COCH$_{2}$CO(CH$_{3}$)$_{3}$

YUBNIS  Asato, E.; Katsura, K.; Mikuriya, M.; Turpeinen, U.; Mutikainen, I.; Reedijk, J. *Inorg. Chem.*
1995, 34, 2447.

**Mean:** 2.460 Å/18 structures

**Eight-coordination**

**CDS codes**

ALINOY, ALOLES, APUSOT, APUSUZ, CEMBAY, CEMBEC, DAPFUX, GEMBEH, HUBKOF, HUBKUL,
HUBLAS, JAXCEQ, JAXGQ, JIVTOY, LIPREI, LOHDUI, OQAPIG, NASZAK, NEDKUD, PURLAP,
PURLAP01, VEFPIG, VEFQIH, WOPVEC, ZAWXAW

**Mean:** 2.458 Å/25 structures
Nine-coordination

*CDS codes*

BOFBII, CEMBEC, DABHOE, DACDIW, DACDOC, EVUDDO, FOVXIX, IPASOH, KOKZOZ, KOZGEP, LENVIK, LOHDES, NEDKUD, OFIDAJ, PEQTOV, PEYREQ, SEYHOV, VEFPIG, WARTAL, XAFBAJ, XAFBIR, ZAWWUP, ZEZTUTM, ZEZTUT01

Mean 2.520 Å/24 structures
**Figure S1.** Calculated conditional stoichiometric constants for the Bi$^{3+}$-oxalate and Bi$^{3+}$-glycine systems as a function of pH. Blue lines represent $K_{E1}$ and orange $K_{E2}$ (Table S2). $K_{E1}=K_1/(\alpha_M \alpha_H)$ and $K_{E2}=K_2/(\alpha_M \alpha_H)$ where $K_1$ is the stoichiometric stability constant, $\alpha_M$ represents the competition from the hydrolysis of the metal ion to the complex formation and is expressed as $\alpha_M = 1+K_1[OH^-]+\beta_{6,12}[Bi^{3+}]$ using the stability constants given in Table S1, ref 1, and $\alpha_H$ represent the competition from the hydrogen ion concentration in the solution (pH) and is expressed as $\alpha_H = 1+K_1[H^+]$ where $K_1$ and $K_2$ stability constants formation of the protonated form of the ligand. For oxalate the following stability constants were used, $K_1=1.88\cdot10^4$ mol$^{-1}$ L and $K_2=18.9$ mol$^{-1}$ L (Kettler, R.; Palmer, D.; Wesolowski, D. Dissociation quotients of oxalic acid in aqueous sodium chloride media to 175°C. *J. Solution Chem.* 1991, 20, 905-927) and for glycine the following stability constants were used, $K_1=3.80\cdot10^9$ mol$^{-1}$ L and $K_2=219$ mol$^{-1}$ L (Borghesani, G.; Pulidori, F.; Remelli, M.; Purrello, R.; Rizzarelli, E. Non-covalent interactions in thermodynamic stereoselectivity of mixed-ligand copper(II)-D- or L-histidine complexes with L-amino acids. A possible model of metal ion-assisted molecular recognition. *J. Chem. Soc., Dalton Trans.* 1990, 2095-2100.)
Figure S2. Specific UV absorbance of DOM as a function of pH in the batch experiments with the organic soil sample. Specific UV absorbance is equal to the UV absorbance measured at $\lambda=254$ nm normalized to mg carbon.
Figure S3. Experimental raw data and model fits of bismuth(III) in soil at different pH values; experimental data (black line), calculated model with parameters given in Table 1 (red line), individual contributions of short Bi-O bond (blue line), long Bi-O bond (green line), Bi···C distance (yellow line), Bi-O-C three-leg scattering (brown line) and Bi···Bi distance (purple line).
Figure S4. Wavelet transform (WT) results for EXAFS data (left column) and model output (right column) using structural parameters in Table 1 ($\kappa = 12$, $\sigma = 2$, $k$ range: 2.8-8 Å$^{-1}$ for pH 1.2, 2.8-10 Å$^{-1}$ for all others). High-intensity areas at $R + \Delta R \approx 3.5$ Å$^{-1}$ are consistent with a Bi–Bi interaction at 4.0 Å$^{-1}$. The WT:s were made using the Igor Pro procedure of M. Chukalina (Wavelet2. ipf, a procedure for calculating the Wavelet transform in IGOR Pro, Grenoble, France, 2010).
Figure S5. (a) XRD patterns of metallic Bi samples subjected to corrosion in pure aqueous solutions (Bi-H$_2$O) and in aqueous solutions with 100 mg L$^{-1}$ fulvic acid (Bi-FA-M). Reference data are from PDF-2 database. (b) Comparison of the background-subtracted diffractograms of for Bi-H$_2$O and Bi-FA-M (characteristic peaks for Bi$_2$O$_3$ and Bi$_2$O$_2$CO$_3$ are indicated for comparison). Background related to X-ray scattering was removed applying polynomial Bezier approximation in Bruker DIFFRAC.EVA v.12 program package (see www.bruker.com/xrd-software).
Figure S6. Metallic Bi samples subjected to corrosion in pure aqueous solutions and in aqueous solutions with 100 mg L\(^{-1}\) fulvic acid.