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A new dodecanuclear bismuth polyaminocarboxylate complex with 2-hydroxy-1,3-diaminopropanetetraacetic acid

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Abstract

A new dodecanuclear Bi(III) complex with 2-hydroxy-1,3-diaminopropanetetraacetic acid (H_5hpdta) corresponding to the stoichiometry $Bi_{12}(H_2hdtpa)_4(Hhdtpa)_6$ was obtained from Bi(III) oxocarbonate and the starting polyaminocarboxylic acid. The crystal structure revealed the presence of two asymmetric parts containing six Bi atoms, each of which displays a ninefold coordination. The involvement of the central hydroxo group in Bi coordination is assumed to be responsible for the peculiarities of this unique structure: the simultaneous involvement of one of the ligands in the coordination of two Bi atoms, the presence of Bi atoms bridged by either one, or three oxygens at the same time, the presence of bridging bidentate (μ_2:η^1:η^2) carboxylates, and direct coordination of Bi(III) to water molecules.

Keywords: Bismuth; Polyaminocarboxylate; hpdta; Crystal structures

1. Introduction

Bismuth, which is the heaviest stable element in the periodic table, displays a marked propensity for high coordination numbers; its complexes with high denticity ligands like polyaminocarboxylic acids generate therefore a peculiar interest in exploring the coordination chemistry of this element. Bi(III) complexes involving organic ligands with pnictogen or chalcogen donors were reviewed recently by Briand and Burford [1]. The molecular and crystal structures of a large number of polyaminocarboxylate (PAC) complexes of Bi(III) have been reported. In particular, we described some years ago the first example of a tenfold coordinated Bi atom in a PAC complex based on the decadentate ttha ligand [2]. Apart from the fundamental aspects related to the variety and peculiarities of their structures, these compounds also generate an increasing interest as molecular solid state precursors for the synthesis of Bi-based inorganic materials. In recent investigations [3], we demonstrated that the association of analogous Bi(III) and La(III) or Pr(III) PAC complexes was a convenient route to the preparation of $Bi_{2-x}Ln_xO_3$ solid solutions displaying the fluorite-like structure of δ-Bi_2O_3, which is to date the best ion conductor known. Within the frame of these studies, the ttha ligand deserved the largest attention because in its fully deprotonated form, its six carboxylic groups can actually accommodate two different metal atoms in their tervalent state. True heteronuclear Bi–Ln complexes corresponding to the formula BiLn(ttha) could therefore be isolated [4] and were shown to be ideal precursors for the synthesis of homogeneous ternary Bi–Ln–O oxides [3]. During the course of further investigations with 2-hydroxy-1,3-diaminopropane–tetraacetic acid (H_5hpdta), the title compound was isolated. This dodecanuclear complex is a unique example which differs structurally from the situation encountered in the only other dodecanuclear Bi complex ever crystallized, i.e. the oxo-citrate com-

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pound $(NH_4)_{12}[Bi_{12}O_8(cit)_8](H_2O)_{10}$ described by Asato et al. [5].

2. Experimental

2.1. Synthesis

Bismuth oxocarbonate (0.79 g, 1.55 mmol) was added to 500 ml of a boiling aqueous solution of H_5hdtpa (1 g, 3.10 mmol). The obtained suspension was heated under stirring until almost complete dissolution. The solid residue was filtered off and the collected filtrate was evaporated slowly at room temperature. After several days, a new solid residue appeared and was again filtered off and the filtrate was allowed to evaporate at room temperature for several weeks. About 1 month later, crystals corresponding to a Bi/ligand ratio of 6/5 were collected. Crude crystals were dried before chemical analysis. Elemental analysis: Exp (%). C, 22.00; H, 2.96; N, 4.39. Calc. for $Bi_{12}(H_2hdtpa)_4(Hhdtpa)_6 \cdot 20H_2O$ (%): C, 21.82; H, 3.06; N, 4.63. Water content: Exp. (TGA): 6.0%, Calc. 5.95%.

2.2. Crystal structure determination

A first data set was collected at room temperature with a four circle diffractometer using four different crystals. Once the surprisingly big structure was solved, it appeared necessary to collect at low temperature using an area detector because water molecules could not be located in the data at room temperature. The crystal ($0.40 \times 0.36 \times 0.30$ mm) was mounted in inert oil and transferred quickly to the cold gas stream (100 K) of a MAR345 image plate equipped with Mo Kα graphite monochromatized radiation ($\lambda = 0.71069$ Å). A total of 188 images at $\Delta\phi$ of 2° and at crystal to detector distance of 120 mm were collected. After integration of the spots the data set included 286 280 reflections of which 30 002 were independent. Crystal data and refinement parameters are summarized in Table 1. The structure was solved by the Patterson methods [6], which revealed the six independent Bi atoms, followed by difference Fourier synthesis. It was refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all the non-hydrogen atoms except the highly agitated water molecules labelled O42–O46 which were refined isotropically [7]. The H atoms of the ligand were calculated and included in the refinement with a common isotropic temperature factor ($U = 0.050$ Å^2). The hydrogen atoms of the 46 water molecules were not located. The largest peaks in the final Fourier difference are located near the heavy atoms.

Table 1
Crystal data of $[Bi_{12}(H_2hpdta)_4(Hhpdta)_6(H_2O)_{12}].80H_2O$

Empirical formula	$C_{110}H_{364}Bi_{12}N_{20}O_{182}$
Formula weight	7387.98
Temperature (K)	100(2)
Wavelength (Å)	0.71069
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	47.720(19)
b (Å)	22.490(10)
c (Å)	32.320(15)
α (°)	90.00(3)
β (°)	129.46(3)
γ (°)	90.00(3)
V (Å^3)	26780(21)
Z	4
D_{calc} (Mg m^{-3})	1.832
Absorption coefficient (mm^{-1})	7.967
$F(000)$	14319
Crystal size (mm)	$0.40 \times 0.36 \times 0.30$
θ max (°)	27.53
Limiting indices	$0 \le h \le 61$, $0 \le k \le 29$, $-41 \le l \le 32$
Reflections collected/unique	286 280/30 002 [$R_{int} = 0.089$]
Completeness to $\theta = 27.53$	97.2%
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	30 002/246/1438
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0559$ [27 688], $wR_2 = 0.1505$
R indices (all data)	$R_1 = 0.0589$, $wR_2 = 0.1536$
Extinction coefficient	0.000248(10)
Largest difference peak and hole (e Å^{-3})	2.731 and −4.495

3. Characterization

Infrared bands assigned to the stretching modes of the carboxylic groups appear at 1619 and 1736 cm^{-1}. The first value is assigned to ionized groups, while the second one reflects the presence of protonated carboxylic groups (in the free H_5hpdta ligand, this band appears at 1718 cm^{-1}).

The thermogravimetric analysis of the title compound shows essentially three degradation steps, corresponding to dehydration (65–135 °C and 135–215 °C), ligand pyrolysis (235–285 °C and 285–310 °C) and final conversion of the carbonate-type intermediates into α-Bi_2O_3, in three successive steps (310–405 °C, 405–415 °C, 415–465 °C).

4. Crystal structure of $[Bi_{12}(H_2hpdta)_4(Hhpdta)_6(H_2O)_{12}] \cdot 80H_2O$

The main crystallographic data are listed in Table 1. The asymmetric part of the unit cell contains six Bi atoms, five ligand molecules and 46 water molecules. A first series of measurements carried out at room

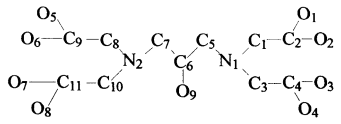
temperature allowed us to locate 29 of these water molecules, the 17 remaining ones being detected after further experiments at 100 K. The water molecules of this second group are highly mobile and loosely bound. The overall unit cell is actually constituted of eight such asymmetric units containing a total of 48 Bi atoms, 40 hpdta molecules and 368 water molecules.

Table 2 lists all Bi–L and Bi–OH_2 coordination bond distances. The Bi atoms were numbered 1–6 and the ligand molecules are identified with the letters A to F. The basic asymmetric unit contains four ligand molecules (A–B–C–D), half of a fifth one (E) and half of a sixth one (F). The atoms of each hpdta ligand are labelled as shown below (Scheme 1).

Ball-shaped independent units made of two asymmetric entities related to each other by a twofold axis (containing the atoms O9E, C6E, O9F and C6F) can be identified. These units contain 12 Bi atoms and 10 hpdta ligands bound to each other by an intricate network of Bi–L and Bi–OH_2 bonds involving bridging water molecules. These two units are connected only by the hydrogen bonds of the water molecules. The labelling of one asymmetric unit and a stereoscopic view of the overall structure gathering two asymmetric subunits are illustrated in Fig. 1(a and b), the water molecules being omitted for clarity.

It is observed that a given ligand molecule can actually be bound through Bi–L bonds to three or four different Bi atoms. In addition, a given Bi atom is always bound to at least two different hpdta moieties and one water molecule. Each Bi atom exhibits a ninefold coordination.

In agreement with previous observations on other Bi complexes described earlier, there is a great discrepancy in the coordination bond distances around the Bi atoms. In the present case, they vary between 2.19 and 3.22 Å. The longest distances are achieved for the atoms Bi2 and Bi3, but are however smaller than 360 pm, which is the sum of the van der Waals radii. Consequently, these bonds can still be considered as effective coordination



Scheme 1.

bonds. Other Bi–L bonds are particularly short (2.2–2.3 Å). The shortest ones (2.19 and 2.21 Å) are included in the same coordination sphere as the longest ones, i.e. around the Bi2 and Bi3 atoms. In spite of this great variety of bond distances, the average coordination distances for each Bi atom are quite similar (from 2.53 to 2.64 Å).

The Bi1 and Bi4 atoms are both coordinated by two halves of different ligand molecules (Bi1: A and B; Bi4: C and D) and an additional water molecule. This half ligand corresponds to bonding through the hydroxo group O9, a nitrogen atom and two acetates linked to this N atom. The remaining four Bi atoms are coordinated by half a ligand, three additional donor atoms belonging to other hpdta moieties and two water molecules. The bond distances involving these four Bi atoms and the half ligands are particularly short (Bi–O < 2.42 Å and Bi–N < 2.47 Å), suggesting rather strong bonding interactions. The Bi–N distances for Bi1 and Bi4 are longer and closer to the usual values.

The coordination mode of certain carboxylate groups is also rather unusual. Two of them (O1D and O6A) are bridging monodentate (μ_2:η^0:η^2, Scheme 2), this resulting in non-equivalent Bi–O distances (2.4 vs. 2.8 Å). Two other carboxylate groups ($-CO_{7D}O_{8D}$ and $-CO_{3A}O_{4A}$) are bidentate and non bridging (μ_1:η^1:η^1, Scheme 3), a coordination mode which is generally absent from the structures of Bi PAC complexes, but rather usual in Bi carboxylates [8]. Here again, the Bi–O distances are quite different (2.5 vs. 3.1 Å), the longest Bi–O bond being associated with the shortest C–O distance and vice versa, as already observed in other structures of Bi carboxylates [9]. These carboxylate groups display the longest Bi–O bond distances ob-

Table 2
Coordination bond distances around Bi atoms (Å) in $Bi_6(H_2hpdta)_2(Hhpdta)_3$

Bi1		Bi2		Bi3		Bi4		Bi5		Bi6	
Bi1–O4B	2.286(5)	Bi2–O9B	2.187(4)	Bi3–O9C	2.212(4)	Bi4–O5C	2.323(5)	Bi5–O9E	2.249(3)	Bi6–O2F	2.262(5)
Bi1–O8A	2.372(4)	Bi2–O8B	2.322(5)	Bi3–O4C	2.287(5)	Bi4–O9C	2.341(4)	Bi5–O2E	2.311(5)	Bi6–O9F	2.272(3)
Bi1–O9B	2.404(4)	Bi2–O6B	2.330(4)	Bi3–O1C	2.416(5)	Bi4–O4D	2.423(5)	Bi5–O3E	2.390(5)	Bi6–O4F	2.381(5)
Bi1–O6A	2.477(4)	Bi2–N2B	2.469(6)	Bi3–N1C	2.429(5)	Bi4–O1D	2.452(5)	Bi5–O1B	2.451(5)	Bi6–N1F	2.455(6)
Bi1–O2B	2.522(4)	Bi2–O8D	2.524(4)	Bi3–O3A	2.481(5)	Bi4–O8C	2.522(5)	Bi5–N1E	2.458(5)	Bi6–O7C [a]	2.464(5)
Bi1–N2A	2.607(5)	Bi2–O2w	2.657(5)	Bi3–O3w	2.825(5)	Bi4–N2C	2.565(6)	Bi5–O1w	2.777(5)	Bi6–O5B	2.793(5)
Bi1–N1B	2.623(6)	Bi2–O6A	2.842(4)	Bi3–O1D	2.855(5)	Bi4–N1D	2.633(6)	Bi5–O1w [a]	2.822(5)	Bi6–O4w [a]	2.803(5)
Bi1–O9A	2.672(5)	Bi2–O7D	3.186(5)	Bi3–O26w	2.869(7)	Bi4–O9D	2.683(5)	Bi5–O2B	2.851(4)	Bi6–O8C [a]	2.869(5)
Bi1–O2w	2.913(5)	Bi2–O8w	3.215(5)	Bi3–O4A	3.080(5)	Bi4–O3w	2.829(5)	Bi5–O2C [a]	2.854(5)	Bi6–O4w	2.932(5)
Bi–L av	2.542	Bi–L av	2.637	Bi–L av	2.606	Bi–L av	2.530	Bi–L av	2.569	Bi–L av	2.581

[a] Symmetry operation $-x+1, y, -z+1/2$.

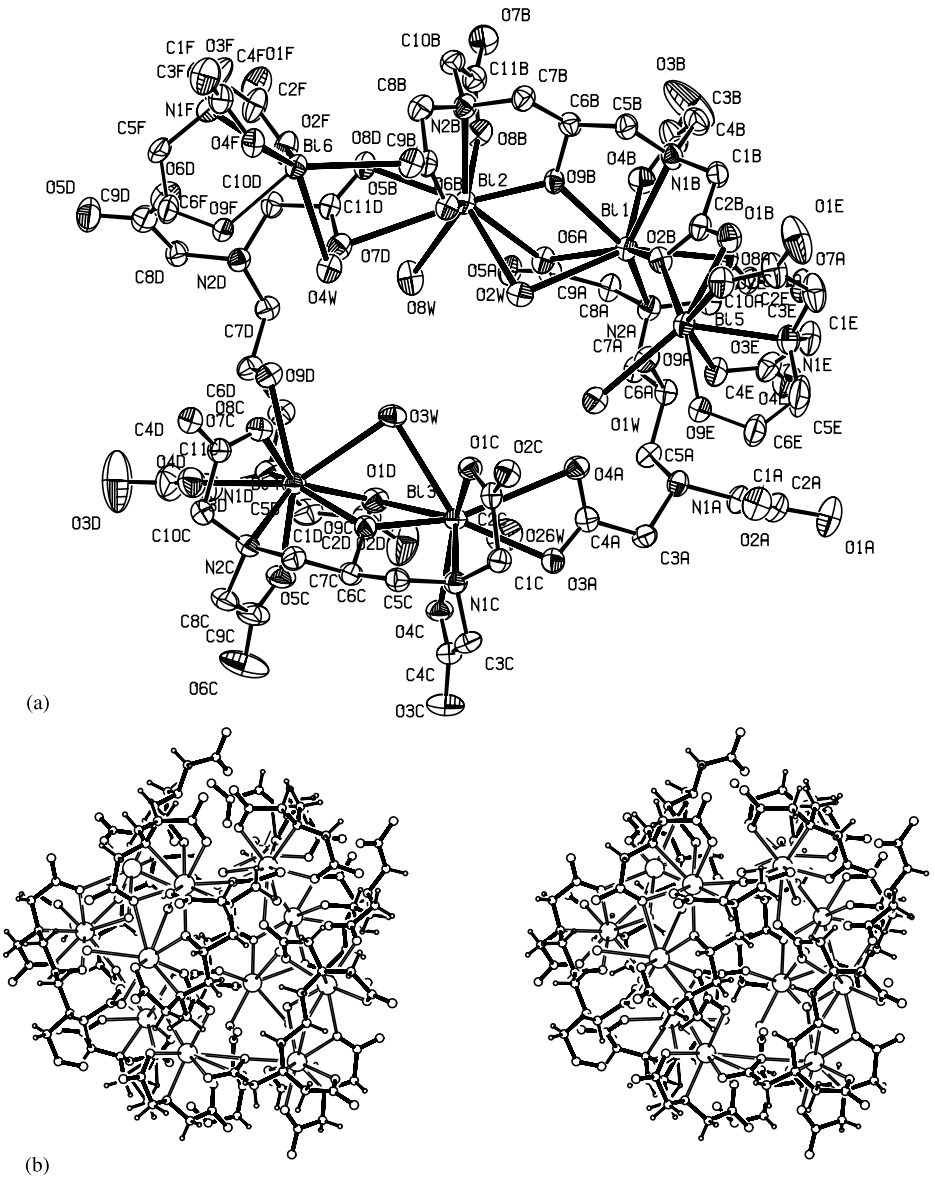
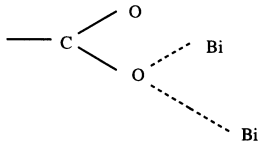
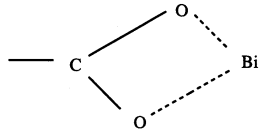


Fig. 1. Labelling of one asymmetric unit (a) and stereoscopic view (b) of $Bi_{12}(H_2hpdta)_4(Hhpdta)_6(H_2O)_{12}$. Additional water molecules have been omitted for clarity [29].

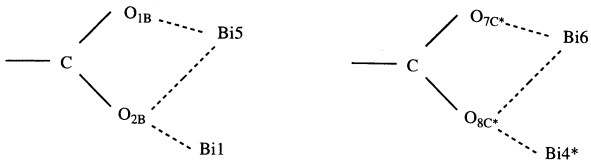


Scheme 2.



Scheme 3.

served. Finally, two other carboxylates ($-CO_{1B}O_{2B}$ and $-CO_{7C}O_{8C}$) adopt a bridging bidentate coordination mode (μ_2:η^1:η^2, Scheme 4), which appears quite particular in the sense that three coordination bonds are involved instead of two [10]. In this case, the two C–O bonds are equivalent. Such a situation was already encountered in the structures of some Bi or lanthanide carboxylates [9–11]. The bond between the bridging oxygen atom (O2B or O8C*) and Bi1 or Bi4* is significantly shorter than that with the second Bi atom (Bi5 or Bi6). Inside this structure, two carboxylate



Scheme 4.

Table 3
C–O bond distances in the carboxylate groups (Å)

A	C–O1A	1.317	C–O3A	1.250	C–O5A	1.267	C–O7A	1.252
	C–O2A	1.221	C–O4A	1.268	C–O6A	1.267	C–O8A	1.283
B	C–O1B	1.275	C–O3B	1.259	C–O5B	1.253	C–O7B	1.224
	C–O2B	1.274	C–O4B	1.271	C–O6B	1.277	C–O8B	1.292
C	C–O1C	1.270	C–O3C	1.259	C–O5C	1.235	C–O7C	1.281
	C–O2C	1.263	C–O4C	1.277	C–O6C	1.271	C–O8C	1.262
D	C–O1D	1.287	C–O3D	1.255	C–O5D	1.341	C–O7D	1.237
	C–O2D	1.230	C–O4D	1.237	C–O6D	1.204	C–O8D	1.284
E	C–O1E	1.256	C–O3E	1.283	C–O5E		C–O7E	
	C–O2E	1.270	C–O4E	1.226	C–O6E		C–O8E	
F	C–O1F	1.232	C–O3F	1.249	C–O5F		C–O7F	
	C–O2F	1.291	C–O4F	1.276	C–O6F		C–O8F	

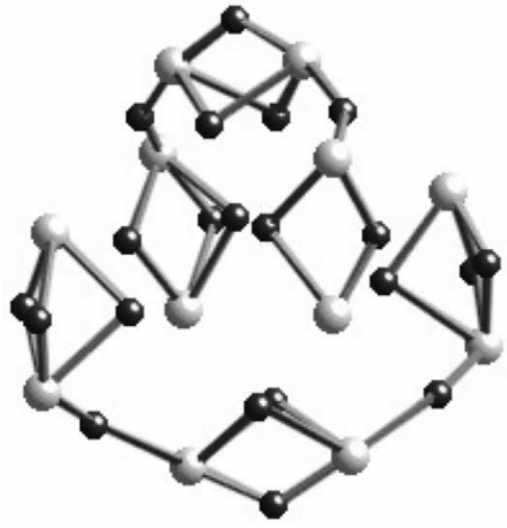
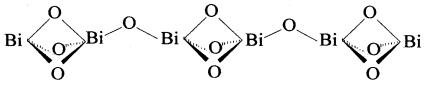


Fig. 2. Schematic view of the semicircular arrangement of the Bi–O chains.



Scheme 5.

groups ($-CO_{1A}O_{2A}$ and $-CO_{5D}O_{6D}$) are not involved in any coordination bond and remain therefore free. From the related C–O distances (Table 3), it can be inferred that these two carboxylate groups are still protonated.

In each independent ball-shaped unit, two chains of six Bi atoms each can be identified, the Bi atoms being linked to each other by bridging oxygen atoms. These chains are folded in a semicircular way, like demilunes which are included in two orthogonal planes, with their open faces in front of each other (Fig. 2). The space between the Bi atoms is filled by three or one bridging oxygen, alternately (Scheme 5).

These two chains are not isolated from each other, in the sense that certain ligand molecules coordinate simultaneously two Bi atoms belonging to each of these chains. It seems that the structural moiety composed of two Bi atoms and three bridging oxygens is rather unique among the crystal structures of the Bi compounds described so far. Such a moiety was reported only in the case of Bi tribenzoate [10] and inside the hexanuclear Bi_6O_{15} center present in the oxoalkoxide $[Bi_6(\mu_3\text{-}O)_3(\mu\text{-}OR)_7(OR)_5]$ $(R = 2,6\text{-}Cl_2C_6H_3)$ [12]. Among the three oxygen atoms in bridging position, there is systematically a O9 type oxygen and one of the four water molecules labelled O1w to O4w.

4.1. Bi-O(hydroxo) bond distances

The two shortest coordination bonds appear between Bi2 and Bi3, on one hand, and the hydroxo oxygen atoms O9B and O9C, on the other hand (2.187 and 2.212 Å, respectively). The Bi–O(hydroxo) bonds reported so far in Bi alkoxides or citrate compounds can actually be quite short, indicating a strong covalent character. For instance, the distances between Bi(III) and a terminal alkoxide are close to 2.1 Å, whereas larger values (from 2.2 to 2.7 Å) characterize the bonds between Bi(III) and a bridging alkoxide in the same structures [13,14]. Similarly, various structures of Bi(III) citrates exhibit Bi–O(hydroxo) distances much shorter (2.12 Å) than Bi–O(carboxylate) bonds [15–17]. Table 4 lists all Bi–O9 bond distances in the title compound. It appears that the bridging hydroxo oxygen atoms are

Table 4
Bi–O9 bond distances (Å)

O9A	–Bi1	2.672
μ-O9B	–Bi1	2.404
	–Bi2	2.187
μ-O9C	–Bi3	2.212
	–Bi4	2.341
O9D	–Bi4	2.683
μ–O9E	–Bi5	2.249
	–Bi5*	2.249
μ-O9F	–Bi6	2.272
	–Bi6*	2.272

involved in shorter distances than the terminal hydroxo groups. The reverse situation was observed in Bi alkoxides. It can be assumed that, in this case, the hydroxo group is nearer to the metal centers because of the simultaneous involvement of the nitrogen atoms and the carboxylate groups from the chelating hpdta ligand bound to the two Bi atoms.

A closer look at Table 4 also reveals that two bonds (Bi1–O9A and Bi4–O9D) are significantly longer than the other ones. The question arises therefore, whether these distances are not indicative of non-deprotonated hydroxo groups C6A–O9A–H and C6D–O9D–H. As described above, five protons are still to be localized in the structure. In the previously reported [18] $(NH_4)[Bi(Hhida)]_2$ complex ($H_3hida = N$-hydroxyethyliminodiacetic acid), in which the two hydroxo groups remain protonated, very long Bi–O distances are observed (2.731 and 2.723 Å), while in the analogous guanidinium (gu) compound [18], $(gu)_2[Bi(Hhida)(hida)]$, in which only one hydroxo group is still protonated, one bond is very short (2.109 Å) and the other one is very long (2.817 Å). Bonds between Bi(III) and R–OH are therefore assumed to be in the range 2.7–2.8 Å, while Bi(III)–RO^- bonds would be expected to be shorter. On the basis of the analogy between the concerned ligands, we suggest that O9A and O9B are still protonated in the title compound. Considering that two protons had already been localized on A and D ligands, three other protons remain to be located.

4.2. Coordination polyhedra around Bi atoms

Although all six Bi atoms are characterized by a ninefold coordination, the coordination polyhedron is not always the same, as a consequence of the different nature of coordinating atoms. The geometry around the Bi1 and Bi4 atoms can be described either as a monocapped square antiprism, or as a tricapped trigonal prism, both slightly distorted. These two possibilities are illustrated in the case of Bi1 in Fig. 3. The square face O9A–O6A–O8A–O4B is capped by the nitrogen atom N2A. The other face O9B–N1B–O2B–O2w is slightly folded due to the occurrence of a somewhat longer bond between Bi1 and O2w.

It is much more difficult to ascribe a regular coordination polyhedron to Bi2 and Bi3. In this case, the wide range of Bi–L distances results in important differences with respect to an idealized geometry. The monocapped square antiprismatic arrangement seems nevertheless to be the most reliable description. One square face appears again much more distorted than the other one. In the case of the antiprismatic geometry, the capping atom is here O6A, and not a nitrogen atom as was always the case in the previously reported Bi PAC complexes. The same dilemma arises for Bi5 and Bi6.

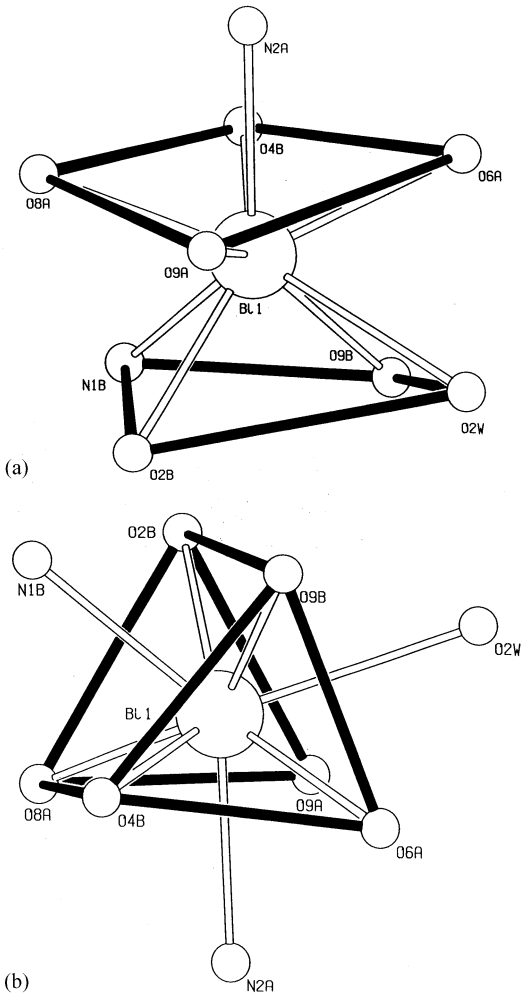


Fig. 3. Coordination polyhedra around Bi1 (a) monocapped square antiprism; (b) tricapped trigonal prism.

4.3. Conformational analysis of the ligands

The overall arrangement of the ligand molecules in this hpdta complex appears to be quite different from that in previously described Bi PAC complexes. There is in the present case no evidence for the classical scheme in which a high denticity ligand molecule was wrapped around a metal atom to generate an isolated metal–ligand moiety. In this hexanuclear Bi hpdta complex, each PAC molecule shares itself between several metal centers.

Fig. 4(a) illustrates the conformation of ligand A. This ligand does not adopt a cation-folded conformation: one half of the ligand is oriented towards a Bi atom, a bidentate carboxylate coordinates another Bi atom, and the last protonated carboxylic group, which is free from any interaction with the metal, is shifted away from the molecule. This description holds also for ligand D. Ligands B and C adopt a totally different "spider-like" conformation that allows them to coordinate 2 Bi atoms simultaneously. This arrangement is not fully

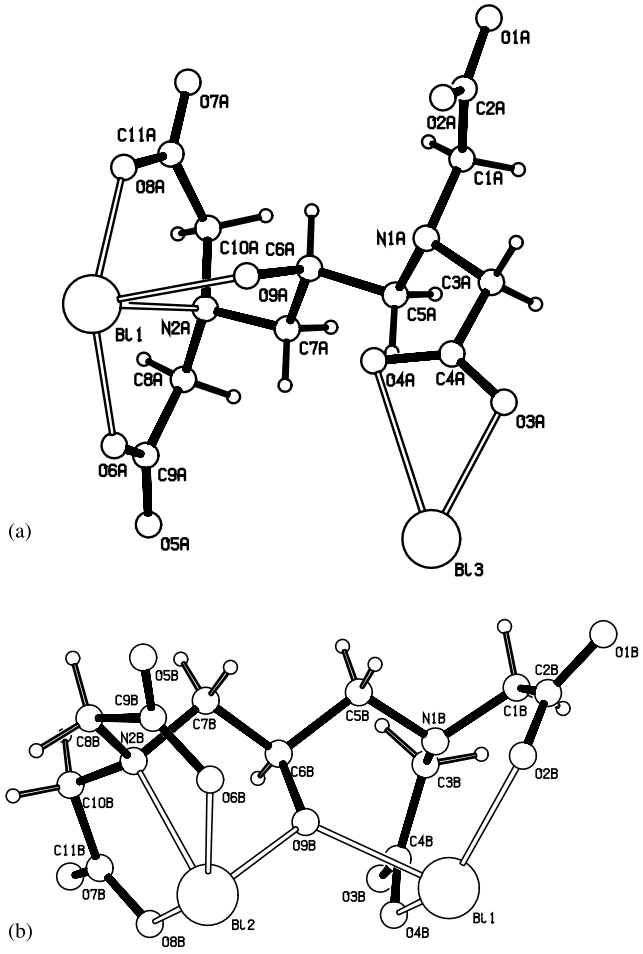


Fig. 4. Ligand conformation around Bi atoms (a) ligand A bound to atoms Bi1 and Bi3; (b) ligand B bound to atoms Bi1 and Bi2.

symmetrical, because one of the Bi atoms is more strongly bound to the ligand than the other one. As shown schematically in Fig. 4(b), wrapping of the ligand around the Bi atom is inhibited by O9.

Ligands E and F exhibit conformations which are very similar to those of ligands B and C. However, the arrangement is in this case perfectly symmetrical, as a consequence of the presence of the twofold axis passing through O9, C6 and in the space between Bi5 and Bi5*. The backbone consisting of N1–C5–C6–C7–N2 and O9 is located in a single plane. Similarly, the two acetate groups attached to a given nitrogen atom (the latter being excluded) are also located in a plane.

The "spider-like" conformation of the hdtpa ligand coordinating simultaneously two metal cations is quite usual in hdtpa complexes and has been reported namely in the following dinuclear compounds: $Na[Ru_2(hpdta)(\mu\text{-}O_2CCH_3)_2]$ [19], $[Fe_2(hpdta)(O_2CCH_2CH{=}CH_2)(H_2O)_2]$ [20], $K_2[V^{III}{}_2(Hhpdta)_2]$ [21], and in the tetranuclear complexes $Na_6[Fe_4(hpdta)_2(O)_2(CO_3)_2]$ [22] and $Ca_2[Mn^{III}{}_3Mn^{II}(\mu_4\text{-}OHO)(Hhpdta)_2(\mu\text{-}O_2CCH_3)_2]$ [23].

The dodecanuclear moiety present in the structure of $Bi_{12}(H_2hpdta)_4(Hhpdta)_6$ is perfectly unique. The only other dodecanuclear unit reported so far is part of the citrate complex crystallized by Asato et al. [5], but this compound exhibits a totally different structure. The oxo-citrato cluster, $Bi_{12}O_{22}$, is the biggest one ever isolated for Bi. This dodecanuclear unit can be subdivided into two hexanuclear $[Bi_6O_4(cit)_4]^{6-}$ subunits, whose structure is very similar to that of the hexanuclear polycationic species $[Bi_6O_4(OH)_4]^{6+}$, which crystallizes from nitrate or perchlorate solutions of Bi(III) [24–28].

5. Conclusions

This new dodecanuclear Bi complex with hdtpa ligand displays a crystal structure with several peculiarities: (i) one of the PAC molecules is not associated with a given Bi atom but is involved simultaneously in the coordination of two Bi(III); (ii) ten ligand molecules surround two chains of six Bi atoms each, in which two Bi atoms are bridged by either one, or three oxygen atoms at the same time; (iii) bridging bidentate carboxylates (μ_2:η^1:η^2) are present in the structure; (iv) some Bi–O bonds are very short; (v) Bi(III) is also directly coordinated to water molecules. It is assumed that these peculiarities are essentially caused by the involvement of the central hydroxo group in Bi coordination.

6. Supplementary material

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 175678. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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