DALTON

Synthesis, characterization and crystal structures of bismuth(III) complexes with triethylenetetraaminehexaacetic acid and *trans*-cyclohexane-1,2-diaminetetraacetic acid

Hilda Wullens,[a] Michel Devillers,*[,a] Bernard Tinant[b] and Jean-Paul Declercq[b]

[a] *Université Catholique de Louvain, Laboratoire de Chimie Inorganique et Analytique,*
place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium
[b] *Université Catholique de Louvain, Laboratoire de Chimie Physique et Cristallographie,*
place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium

Two new water-soluble bismuth(III) complexes with polyaminocarboxylate ligands have been prepared, characterized by IR spectroscopy and crystal-structure analysis. The complex with triethylenetetraaminehexaacetic acid (H_6ttha) has the stoichiometry Bi(H_3ttha)·$3H_2O$ **1**. It crystallizes in the space group *P*2/*c* with two independent $\frac{1}{2}$ (H_3ttha·Bi) units in which the cations are located on the crystallographic two-fold axis. It is the first example of a polyaminocarboxylate complex of Bi^{III} displaying a co-ordination number of ten, through four nitrogen atoms and six oxygens belonging to the acetates. The ligand is wrapped round the cation in a bicapped square-antiprismatic geometry. In the complex with *trans*-cyclohexane-1,2-diaminetetraacetic acid (H_4cydta), Bi(Hcydta)·$5H_2O$ **2**, the co-ordination number is eight with a square-antiprismatic geometry around the Bi. For each Bi atom two of the co-ordinated oxygen atoms belong to neighbouring molecules; these bridging oxygen atoms are different in the two subunits and connect the complexed entities in a polymeric network.

Great interest is devoted nowadays to the co-ordination chemistry of bismuth because of the wide applicability of this element in various research fields like bioinorganic chemistry, oxide-based superconductors, and heterogeneous catalysis. The antacid properties of bismuth salts have actually been used in medicine for more than 200 years in the treatment of ulcers and gastrointestinal disorders. Colloidal bismuth subcitrate (CBS) is the most widely used active component in modern Bi-based pharmaceuticals.[1]

Interest in bismuth chemistry was increased by the discovery by Maeda *et al.*[2] of the high-T_c superconductivity in the Bi–Ca–Sr–Cu–O system, promoting thereby investigations on the use of Bi-based compounds as potential precursors for the manufacture of Bi-containing ceramics. The so-called chelating method,[3] involving low-temperature decomposition of solid metal precursors obtained from a solution of the complexed metals, has proved to be an advantageous way to obtain mixed metal oxides displaying homogeneous composition, and competes efficiently with the conventional ceramic route based on the high-temperature treatment of a mixture of the oxides or carbonates. Since they form stable complexes with a wide range of metals, the most widely used chelating agents are ethylenediaminetetraacetic acid (H_4edta), hydroxyethylethylenediaminetriacetic acid and nitrilotriacetic acid (H_3nta). Analogous procedures involving the use of citric acid (3-carboxy-3-hydroxypentane-1,5-dioic acid) (citrate process) were also used with success, not only in the ceramic field but also for the preparation of oxide-based heterogeneous catalysts.[4–6] In addition, chelate complexes with H_4edta or H_5dtpa (diethylenetriaminepentaacetic acid) were sometimes used as solid-state molecular precursors for the synthesis of Y–Ba–Cu–O superconductors.[7]

From a co-ordination chemistry point of view, a further point of interest in bismuth compounds is related to the potential stereochemical activity of the lone electron pair, giving rise to various structural peculiarities. The synthesis and the crystal structures of several bismuth(III) complexes with H_4edta, H_3nta and H_5dtpa have been already described. These compounds correspond to the following stoichiometries: Bi(nta)$(H_2O)_2$,[8,9] $[NH_4]_3[Bi(nta)_2]$,[10] $[NH_4]_4[Bi(nta)_2(NCS)]$,[9] Bi(Hedta),[11] Bi(Hedta)·$2H_2O$,[8] $[NH_4]$[Bi(edta)]·H_2O,[11] $[CN_3H_6]$[Bi(edta)(H_2O)],[12] K[Bi(Hdtpa)(H_2O)]·$4H_2O$[13] and $[CN_3H_6]_2$[Bi(dtpa)]·$4H_2O$.[8] The starting material is traditionally $Bi(OH)_3$, exceptionally the oxocarbonate $Bi_2O_2(CO_3)$.

We report here the isolation, crystal structures and IR spectroscopic characterization of two new water-soluble bismuth(III) complexes with the polyaminocarboxylate ligands triethylenetetraaminehexaacetic acid [*N*,*N*′-dicarboxyethylenedinitrilobis(ethylenenitrilo)tetraacetic acid] (H_6ttha) and *trans*-cyclohexane-1,2-diaminetetraacetic acid (*trans*-cyclohexane-1,2-diyldinitrilotetraacetic acid) (H_4cydta).

Experimental

Materials

The compounds H_6ttha and H_4cydta and bismuth(III) carbonate dioxide from Fluka were used as received.

Preparations

Bi(H_3ttha)·$3H_2O$ 1. The compound H_6ttha (3 g, 6.07 mmol) was dissolved in water (150 cm^3) upon heating. The oxocarbonate, $Bi_2O_2(CO_3)$ (1.55 g, 3.04 mmol), was added and the mixture heated with stirring for 5 h. Undissolved bismuth oxocarbonate was filtered off whilst hot. The colourless filtrate was allowed to evaporate in the air and crystals of compound **1** appeared on cooling. Drying under vacuum at room temperature for several hours resulted in opaque crystals corresponding to the chemical composition Bi(H_3ttha)·$2H_2O$ (Found: C, 28.70; H, 4.45; N, 7.35. Calc. for $C_{18}H_{31}BiN_4O_{14}$: C, 28.65; H, 4.40; N, 7.45%).

Bi(Hcydta)·$5H_2O$ 2. The compound H_4cydta (1 g, 2.745 mmol) was added to water (100 cm^3) and heated to boiling. The compound $Bi_2O_2(CO_3)$ (0.7 g, 1.373 mmol) was added and

Table 1 Infrared spectroscopic data (cm^{-1}) for the free acids and complexes **1** and **2**

Compound	ν(OH)	ν(CO_2^-)	ν(CO_2H)
H_6ttha	3442 (br)		1737vs 1700 (sh)
1 Bi(H_3ttha)·$2H_2O$	3400s 3293s	1610vs	1703vs 1690s
H_4cydta	3510s		1752, 1730, 1708vs 1656–1586
2 Bi(Hcydta)·H_2O	3435 (br)	1619vs (br)	Masked

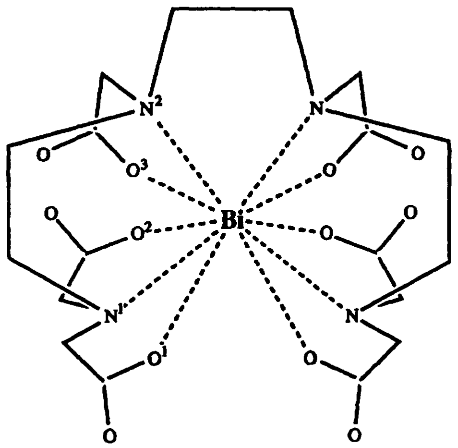


Fig. 1 Schematic drawing of the crystal structure of compound **1**

heated with stirring for at least 2 h. After filtration of the hot solution, the colourless filtrate was allowed to stand at room temperature and crystals of compound **2** appeared after several days. Drying under vacuum at room temperature for several hours caused disintegration of the crystals and the powder obtained corresponded to the chemical composition Bi(Hcydta)·H_2O (Found: C, 29.05; H, 3.80; N, 4.75. Calc. for $C_{14}H_{21}BiN_2O_9$: C, 29.50; H, 3.70; N, 4.90%).

X-Ray crystallography

Crystals sealed in Lindemann glass capillaries were examined at 20 °C on a Huber four-circle diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 69 Å). Crystal measurement and refinement data are summarized in Table 2. The lattice parameters were refined using 30 reflections for compound **1** and 26 for **2** in the range $5 \leqslant 2\theta \leqslant 20°$. Intensities were measured with ω scans. One standard reflection was checked every 50 and no significant deviation was observed. The intensity data were corrected for Lorentz-polarization and for absorption by semiempirical (ψ scans) method. Both structures were solved from Patterson and difference syntheses using the program SHELXS 86.[14] They were refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL 93[15]). It was not possible to locate the H atoms from the Fourier-difference map; and in both structures the H atoms of the methylene groups were calculated, while those of the carboxylic groups were not included in the refinement. The largest peaks in the final difference syntheses were close to the heavy atoms. Atomic scattering factors were taken from ref. 16.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/13.

Results and Discussion

Infrared analysis

The main infrared absorption bands of the free acids and the bismuth(III) complexes are listed in Table 1. Several changes in the IR data in the OH and CO_2H regions occur on formation of compound **1** and result from the ionization of the ligand. The coexistence of ionized and non-ionized carboxylic groups is shown by the presence of characteristic bands at 1610 cm^{-1} and in the region 1690–1705 cm^{-1}. In the IR spectrum of compound **2** the bands characteristic of the non-ionized carboxylic group are assumed to be masked by the very broad absorption band of CO_2^- at 1619 cm^{-1}

Crystal structures

Selected bond lengths and angles in complexes **1** and **2** are presented in Tables 3 (co-ordination distances Bi–O and Bi–N), 4 and 5 (angles around Bi atoms).

Complex 1. Fig. 1 presents a schematic drawing of complex **1**. The triionized ttha acts as a decadentate ligand which co-ordinates the central Bi atom through its four nitrogen atoms and six oxygen atoms belonging to the acetate groups. Nevertheless, the asymmetric part of the unit cell does not correspond to the Bi(H_3ttha) moiety, but to two independent halves of that entity (labelled **1A** and **1B**). The two independent bismuth cations lie on distinct crystallographic two-fold axes at (0, 0.1026, $\frac{1}{4}$) and ($\frac{1}{2}$, 0.9698, $\frac{3}{4}$). The diad axis passes through the midpoint of the central C(9)–C(9*) bond of the ttha molecule. Fig. 2 shows the wrapping of the ligand around Bi for **1A**. The geometry of molecules **1A** and **1B** is essentially the same and, in particular, the conformations of the ttha ligand are very similar. The main difference is the Bi–O(1) distance which is significantly shorter in **1A** [2.694(7) Å] than in **1B** [2.912(7) Å] (see Table 3). There is no clear correlation between the C–O distances in the carboxylic(ate) groups and the involvement of the oxygen atoms in bismuth co-ordination or hydrogen-bond formation (Table 6).

The co-ordination polyhedron (co-ordination number 10) can be best described as a distorted bicapped square antiprism (Fig. 3). This environment is common to the two non-equivalent metal centres. In this structure the two external nitrogen atoms [N(1), N(1′)] are in capping positions, and the square faces are formed by the remaining chelating atoms: N(2), O(3′), O(2), O(1) and N(2′), O(1′), O(2′), O(3). Table 7 lists the root-mean-square (r.m.s.) values of the fitted atoms to the best mean planes and the dihedral angles between these planes for the two Bi atoms.

The overall structure consists of isolated complexes connected to each other through an intricate network of hydrogen bonds involving the three co-crystallized water molecules. Table 8 lists the intermolecular O···O contact distances shorter than 3.2 Å. No intermolecular O···N interaction was observed within this range. One of the water molecules is removed on drying and was not found in the samples submitted to elemental analysis.

Complex 2. Fig. 4 shows the crystal structure of the complex Bi(Hcydta)·$5H_2O$ **2**. There are again two independent complex entities (Hcydta·Bi) in the asymmetric part of the unit cell. The two bismuth atoms are surrounded by eight co-ordinating atoms arranged in a square antiprism. The Hcydta molecule behaves as a hexadentate ligand and the two additional positions are occupied by two oxygen atoms belonging to neighbouring molecules. These two atoms are seen to be different if one compares the surroundings of Bi(1) [O(53′), O(53′^{III})] and Bi(2) [O(3′^{III}), O(52′^{IV})]. Among the four acetate groups, two are in bridging positions and the other two are co-ordinated in a monodentate fashion to a single bismuth. For

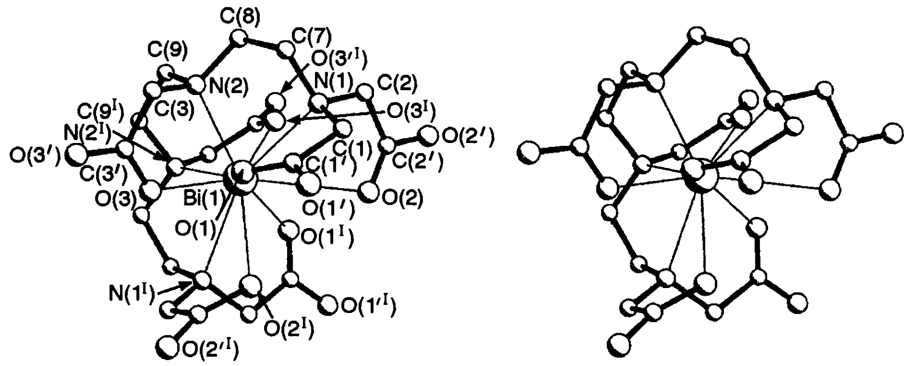


Fig. 2 Stereoscopic view of complex **1A**.[17] Atoms labelled I are related by the symmetry transformation $-x, y, \frac{1}{2} - z$

Table 2 Data collection and refinement parameters*

	1	**2**
Formula	$C_{18}H_{27}BiN_4O_{12}{\cdot}3H_2O$	$C_{14}H_{29}BiN_2O_8{\cdot}5H_2O$
M	754.48	642.37
Crystal system	Monoclinic	Triclinic
Space group	$P2/c$	$P\bar{1}$
a/Å	17.691(3)	12.494(4)
b/Å	8.175(2)	13.924(2)
c/Å	17.782(5)	13.264(7)
α/°		72.52(3)
β/°	102.59(2)	72.75(3)
γ/°		82.59(3)
U/Å^3	2510(1)	2130(2)
F(000)	1476	1244
μ/mm^{-1}	7.11	7.94
Approximate crystal size/mm	0.40 × 0.32 × 0.20	0.40 × 0.28 × 0.08
hkl Ranges	0–22, 0–10, −23 to 23	0–15, −17 to 18, −16 to 17
Standard reflection	6 −1 0	−3 −3 2
No. reflections	6344	9752
No. observed reflections [$I \geqslant 2\sigma(I)$]	3577	5766
No. parameters	346	542
Minimum, maximum transmission factors	0.9248, 1.0421	0.6701, 1.3611
R ($I \geqslant 2\sigma I$)	0.059	0.062
(all data)	0.102	0.115
$wR2$	0.119	0.136
w	$1/[\sigma(F_o)^2 + 0.0686P^2]$	$1/[\sigma(F_o)^2 + 0.0811P^2]$
S	0.923	0.928
Extinction parameter	0.0048	None
Maximum shift/e.s.d.	0.001	0.002
Maximum, minimum residual density/e Å^{-3}	2.39, −1.59	1.99, −2.49

* Details in common: $Z = 4$; $D_c = 2.00$ g cm^{-3}; maximum ($\sin\theta$)/λ 0.65 Å^{-1}

Table 3 Co-ordination bond lengths (Å) in complexes **1** and **2**

	1A	**1B**		**2**		
Bi–O(1)	2.694(7)	2.912(7)		2.584(10)	–O(51)	2.497(11)
Bi–O(2)	3.055(8)	2.988(8)		2.286(9)	–O(52)	2.404(9)
Bi–O(3)	2.320(7)	2.327(7)		2.439(9)	–O(53)	2.454(8)
Bi–O(4)				2.339(9)	–O(54)	2.431(10)
Bi–O			–O(53')	2.695(9)	–O($3'^{\mathrm{III}}$)	2.617(11)
Bi–O			–O($53'^{\mathrm{III}}$)	2.916(10)	–O($52'^{\mathrm{IV}}$)	2.612(9)
Bi–N(1)	2.813(8)	2.803(8)		2.512(11)	–N(51)	2.513(10)
Bi–N(2)	2.473(9)	2.472(8)		2.491(11)	–N(52)	2.504(11)

Symmetry transformations: III $-x, -y, -z + 1$; IV $-x + 1, -y - 1, -z + 1$.

Bi(1) the square faces are delimited by O(4), N(2), O(3), O($53'^{\mathrm{III}}$) and O(2), N(1), O(1), O(53'), respectively [Fig. 5(*a*)]. For Bi(2) they are delimited by O(52), O($52'^{\mathrm{IV}}$), O(51), N(51) and O(54), O($3'^{\mathrm{III}}$), O(53), N(52), respectively [Fig. 5(*b*)]. The r.m.s. values of the fitted atoms to the mean planes, distances of Bi from these planes and their dihedral angles are listed in Table 7.

The conformation of the Hcydta molecule is similar in the two independent complex entities and, except for one C–C–N–C torsion angle, is the same as that observed for the free acid.[18]

Ten water molecules have been located in the structure. They are all involved in a hydrogen-bonding network for which intermolecular O···O contact distances are summarized in Table 8.

General comments

Crystallographic data characteristic of various polyaminocarboxylate complexes of Bi$^{\mathrm{III}}$ previously described are presented in Table 9. In the complexes described so far the bismuth co-

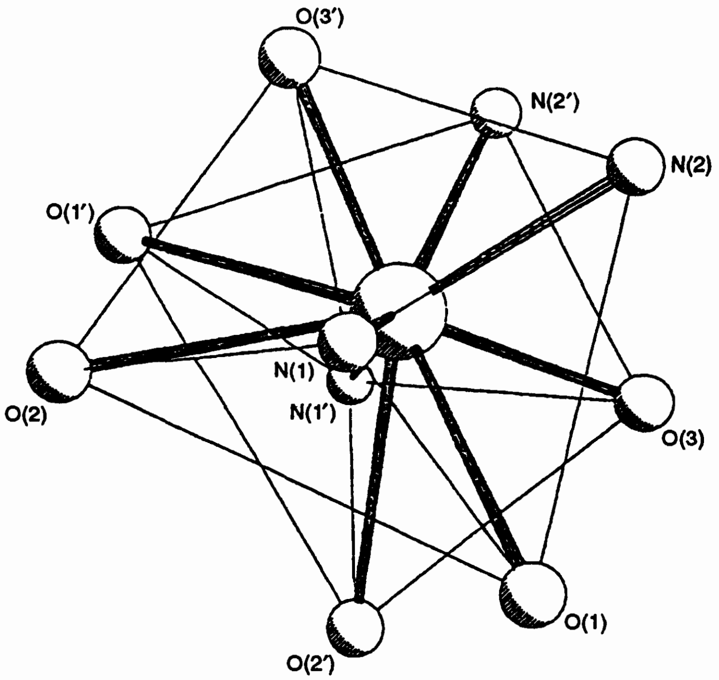


Fig. 3 Co-ordination polyhedron around Bi in complex **1A**[17]

Table 4 Bond angles (°) around Bi in complex **1**

	1A	**1B**
O(3$^{\mathrm{I}}$)–Bi(1)–O(3)	134.2(4)	136.5(4)
O(3$^{\mathrm{I}}$)–Bi(1)–N(2$^{\mathrm{I}}$)	70.0(3)	70.2(2)
O(3)–Bi(1)–N(2$^{\mathrm{I}}$)	73.9(3)	75.5(3)
N(2$^{\mathrm{I}}$)–Bi(1)–N(2)	75.0(4)	74.6(4)
N(2)–Bi(1)–O(1$^{\mathrm{I}}$)	138.3(3)	139.0(2)
O(3)–Bi(1)–O(1)	67.1(2)	66.1(2)
N(2)–Bi(1)–O(1)	78.3(3)	79.5(2)
O(1$^{\mathrm{I}}$)–Bi(1)–O(1)	139.9(3)	137.8(3)
O(3$^{\mathrm{I}}$)–Bi(1)–N(1)	73.8(2)	76.4(2)
O(3)–Bi(1)–N(1)	116.8(3)	113.3(2)
N(2$^{\mathrm{I}}$)–Bi(1)–N(1)	134.6(3)	135.2(3)
N(2)–Bi(1)–N(1)	69.3(3)	68.6(3)
O(1$^{\mathrm{I}}$)–Bi(1)–N(1)	111.5(2)	113.1(2)
O(1)–Bi(1)–N(1)	58.8(2)	56.7(2)
N(1)–Bi(1)–N(1$^{\mathrm{I}}$)	154.6(4)	154.9(4)
O(3$^{\mathrm{I}}$)–Bi(1)–O(2)	72.8(2)	71.8(2)
O(3)–Bi(1)–O(2)	151.7(2)	150.1(2)
N(2$^{\mathrm{I}}$)–Bi(1)–O(2)	132.6(3)	133.1(2)
N(2)–Bi(1)–O(2)	121.0(3)	120.5(2)
O(1$^{\mathrm{I}}$)–Bi(1)–O(2)	60.5(2)	60.3(2)
O(1)–Bi(1)–O(2)	88.7(2)	87.5(2)
N(1)–Bi(1)–O(2)	55.3(2)	56.2(2)
N(1$^{\mathrm{I}}$)–Bi(1)–O(2)	103.8(2)	103.4(2)
O(2)–Bi(1)–O(2$^{\mathrm{I}}$)	82.6(3)	83.1(3)

Symmetry transformation: I $-x, y, -z + \frac{1}{2}$.

ordination number is usually eight, with various co-ordination polyhedra. Despite the fact that some authors have described the Bi–edta complexes as having different co-ordination geometries,[8,11] careful re-examination of the published structures suggests that all three complexes can be described with the same model, *i.e.* square antiprismatic. A co-ordination number of nine is reached in the case of dtpa (compounds **10** and **11** in Table 9) or when an additional ligand is present in the co-ordination sphere (thiocyanate in **5**).

Compound **2** displays a coordination number of eight, in line with the pronounced analogy between the Hcydta and Hedta ligands. Compound **1** is the first example of a polyaminocarboxylate complex with a co-ordination number of 10. Such a high value had been observed in bismuth complexes with polyethylene glycols or crown ethers, showing various kinds of co-ordination polyhedra.[19] In our case this structure is directly related to the decadentate nature of the ttha ligand. In most of these compounds the attainment of a high co-ordination

Table 5 Bond angles (°) around Bi in complex **2**

O(2)–Bi(1)–O(4)	76.6(3)	O(52)–Bi(2)–O(54)	76.7(3)
O(2)–Bi(1)–O(3)	147.6(3)	O(52)–Bi(2)–O(53)	143.9(3)
O(4)–Bi(1)–O(3)	111.1(3)	O(54)–Bi(2)–O(53)	110.8(3)
O(2)–Bi(1)–N(2)	88.9(4)	O(52)–Bi(2)–N(52)	86.0(3)
O(4)–Bi(1)–N(2)	68.2(3)	O(54)–Bi(2)–N(52)	68.5(3)
O(3)–Bi(1)–N(2)	67.0(3)	O(53)–Bi(2)–N(52)	66.1(3)
O(2)–Bi(1)–N(1)	68.7(3)	O(52)–Bi(2)–N(51)	67.2(3)
O(4)–Bi(1)–N(1)	127.0(3)	O(54)–Bi(2)–N(51)	128.0(3)
O(3)–Bi(1)–N(1)	83.0(3)	O(53)–Bi(2)–N(51)	82.4(3)
N(2)–Bi(1)–N(1)	72.2(3)	N(52)–Bi(2)–N(51)	72.8(3)
O(2)–Bi(1)–O(1)	104.6(3)	O(52)–Bi(2)–O(51)	105.9(4)
O(4)–Bi(1)–O(1)	165.9(3)	O(54)–Bi(2)–O(51)	165.1(3)
O(3)–Bi(1)–O(1)	75.7(3)	O(53)–Bi(2)–O(51)	76.1(3)
N(2)–Bi(1)–O(1)	125.5(3)	O(51)–Bi(2)–N(52)	126.0(3)
N(1)–Bi(1)–O(1)	65.0(3)	O(51)–Bi(2)–N(51)	65.0(3)
O(2)–Bi(1)–O(53′)	73.2(3)	O(52)–Bi(2)–O(52$'^{\mathrm{IV}}$)	73.1(3)
O(4)–Bi(1)–O(53′)	85.7(3)	O(54)–Bi(2)–O(52$'^{\mathrm{IV}}$)	83.3(4)
O(3)–Bi(1)–O(53′)	137.1(3)	O(53)–Bi(2)–O(52$'^{\mathrm{IV}}$)	141.4(3)
N(2)–Bi(1)–O(53′)	151.3(3)	O(51)–Bi(2)–O(52$'^{\mathrm{IV}}$)	83.5(4)
N(1)–Bi(1)–O(53′)	119.0(3)	N(52)–Bi(2)–O(52$'^{\mathrm{IV}}$)	148.2(4)
O(1)–Bi(1)–O(53′)	81.4(3)	N(51)–Bi(2)–O(52$'^{\mathrm{IV}}$)	117.9(3)
O(2)–Bi(1)–O(53$'^{\mathrm{III}}$)	143.4(3)	O(52)–Bi(2)–O(3$'^{\mathrm{III}}$)	141.5(3)
O(4)–Bi(1)–O(53$'^{\mathrm{III}}$)	92.4(3)	O(54)–Bi(2)–O(3$'^{\mathrm{III}}$)	88.4(3)
O(3)–Bi(1)–O(53$'^{\mathrm{III}}$)	69.0(3)	O(53)–Bi(2)–O(3$'^{\mathrm{III}}$)	74.6(3)
N(2)–Bi(1)–O(53$'^{\mathrm{III}}$)	119.7(3)	O(51)–Bi(2)–O(3$'^{\mathrm{III}}$)	80.6(3)
N(1)–Bi(1)–O(53$'^{\mathrm{III}}$)	138.4(3)	N(52)–Bi(2)–O(3$'^{\mathrm{III}}$)	121.4(3)
O(1)–Bi(1)–O(53$'^{\mathrm{III}}$)	78.3(3)	N(51)–Bi(2)–O(3$'^{\mathrm{III}}$)	142.3(3)
O(53′)–Bi(1)–O(53$'^{\mathrm{III}}$)	71.2(3)	O(52$'^{\mathrm{II}}$)–Bi(2)–O(3$'^{\mathrm{III}}$)	69.9(3)

Symmetry transformation: II $-x + 1, y, -z + \frac{3}{2}$.

Table 6 Bond lengths (Å) in the carboxylic (ate) groups

	1A	**1B**	**2A**		**2B**
C(1′)–O(1)	1.234(12)	1.221(12)	1.22(2)	–O(51)	1.22(2)
C(1′)–O(1′)	1.298(11)	1.281(12)	1.31(2)	–O(51′)	1.31(2)
C(2′)–O(2)	1.209(12)	1.220(12)	1.28(2)	–O(52)	1.28(2)
C(2′)–O(2′)	1.319(13)	1.311(12)	1.26(2)	–O(52′)	1.24(2)
C(3′)–O(3)	1.274(13)	1.282(12)	1.27(2)	–O(53)	1.30(2)
C(3′)–O(3′)	1.244(13)	1.214(12)	1.23(2)	–O(53′)	1.246(14)

Table 7 Root-mean-square values of the fitted atoms to the mean planes and dihedral angles around Bi atoms[15]

	1		2	
	Bi(1A)	Bi(1B)	Bi(1)	Bi(2)
R.m.s. plane 1	0.013	0.066	0.145	0.140
R.m.s. plane 2	0.074	0.058	0.145	0.140
Dihedral angles between 1–2/°	4	6	3	4
Distances/Å of Bi to plane 1	1.31	1.29	1.18	1.19
Bi to plane 2	−1.39	−1.38	−1.18	−1.19

Table 8 Hydrogen bonds in the structures of compounds **1** and **2**: O ··· O contact distances (Å) less than 3.2 Å (σ = 0.01 Å)

1		**2**			
O(1A) ··· O(1′B^{I})	3.19	O(1′) ··· O(54′^{VI})	2.52	O(1w) ··· O(2w)	2.67
O(1′A) ··· O(1′B^{I})	2.49	O(2′) ··· O(1w)	2.67	O(1w) ··· O(3w)	2.76
O(1′A) ··· O(3w)	3.00	O(3) ··· O(53^{VII})	3.05	O(1w) ··· O(8w^{VII})	2.72
O(1′A) ··· O(2w^{II})	3.02	O(3′) ··· O(3w^{VIII})	2.81	O(3w) ··· O(5w)	2.91
O(2′A) ··· O(1w)	2.60	O(3′) ··· O(52′^{IX})	3.00	O(3w) ··· O(7w^{XI})	2.80
O(3′A) ··· O(1w^{III})	2.72	O(3′) ··· O(53^{VII})	3.08	O(4w) ··· O(7w)	2.84
O(1w) ··· O(1′B^{IV})	2.72	O(4′) ··· O(6w^{X})	2.80	O(4w) ··· O(5w^{II})	2.78
O(2′B) ··· O(2w)	2.61	O(4′) ··· O(8w^{XI})	2.82	O(4w) ··· O(4w^{XIV})	3.02
O(2′B) ··· O(3w^{II})	3.19	O(51) ··· O(5w^{X})	3.09	O(6w) ··· O(7w)	2.69
O(1B) ··· O(3w^{XV})	2.83	O(51′) ··· O(2w)	2.50	O(8w) ··· O(9w)	2.85
O(3′B) ··· O(2w^{XV})	2.82	O(52) ··· O(5w^{XII})	2.97		
O(3′B) ··· O(3w^{XV})	2.94	O(52) ··· O(52^{XIII})	3.05		
O(2w) ··· O(3w^{II})	3.04	O(52′) ··· O(52^{XIII})	2.99		
		O(53) ··· O(2w^{X})	2.78		
		O(53′) ··· O(2)	2.99		
		O(53′) ··· O(3^{VII})	3.06		
		O(54) ··· O(10w^{XII})	2.99		
		O(54′) ··· O(10w^{VII})	2.95		

Symmetry transformations: I $x, 1 - y, z - \frac{1}{2}$; II $1 - x, 1 - y$; III $-x, y - 1, \frac{1}{2} - z$; IV $-x, 1 - y, 1 - z$; V $1 - x, 1 + y, \frac{3}{2} - z$; VI $x, 1 + y, z$; VII $-x, -y, 1 - z$; VIII $x - 1, y, z$; IX, $x - 1, 1 + y, z$; X $1 - x, -y, 1 - z$; XI $x, y, z - 1$; XII $x, y - 1, z$; XIII $1 - x, -1 - y, 1 - z$; XIV $1 - x, 1 - y, 2 - z$; XV $x, 1 - y, \frac{1}{2} + z$.

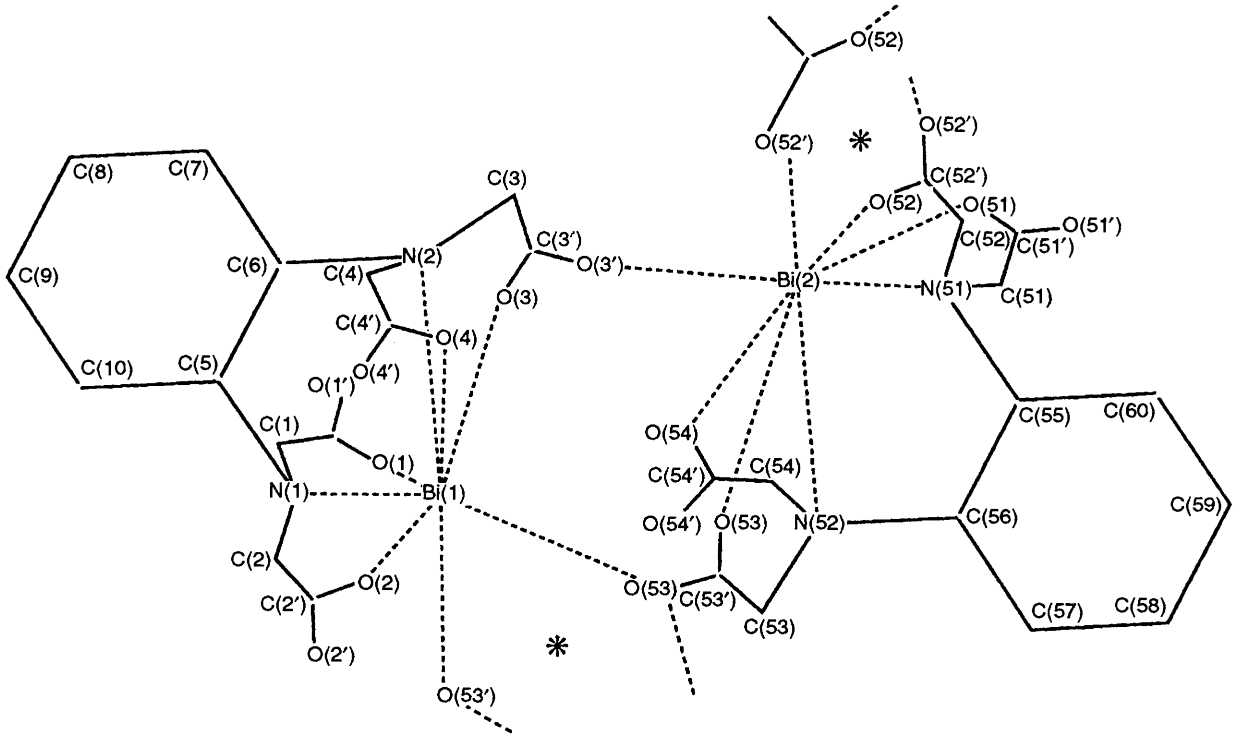
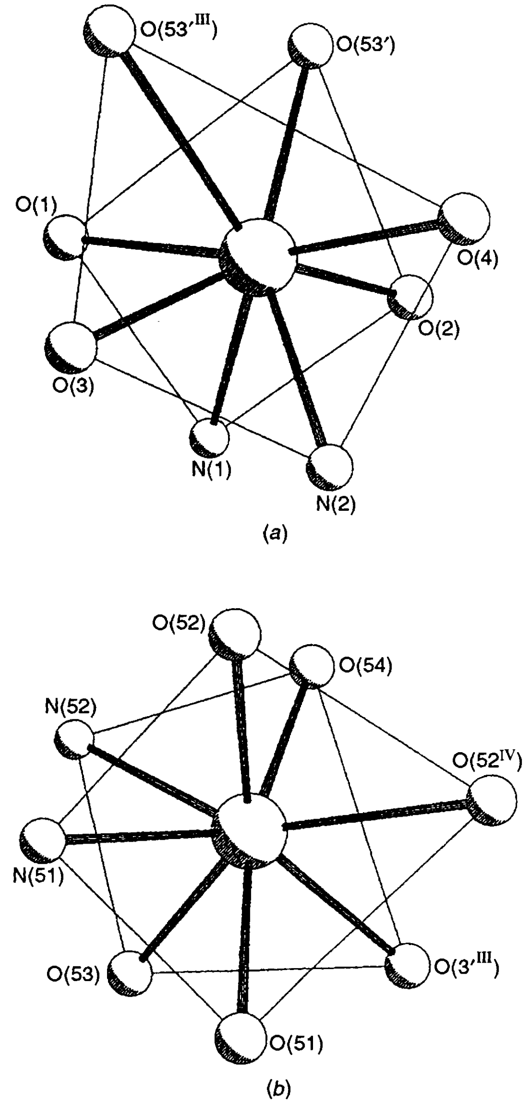


Fig. 4 Schematic drawing of the crystal structure of compound **2**

number requires atoms from neighbouring molecules to be involved in the co-ordination sphere, resulting in the occurrence of a polymeric network. A comparison of the structures of the bismuth complexes with edta, dtpa and ttha ligands shows a regular increase in co-ordination number from eight to 10, achieved by incorporating additional nitrogen atoms in capping positions, converting thereby the initial square antiprism into a monocapped, then bicapped polyhedron. Simultaneously, the number of oxygen atoms from outside decreases. In the edta complexes **6–9** and the dtpa complex **11**, the formation of the

Table 9 Comparative crystallographic data for bismuth(III) complexes with various polyaminocarboxylate ligands

	Complex	Co-ordination number	Co-ordination polyhedron	Ref	Bi–O/Å Minimum	Bi–O/Å Maximum	Bi–N/Å
1	Bi(H_3ttha)·$3H_2O$	10	Bicapped square antiprism	This work	2.32–2.33	3.05–2.99	2.47–2.81
2	Bi(Hcydta)·$5H_2O$	8	Square antiprism	This work	2.29–2.40	2.92–2.62	2.49–2.51
3	$[NH_4]_3$[Bi(nta)$_2$]	8	Bicapped trigonal prism	10	2.40	2.44	2.58–2.60
4	[Bi(nta)(H_2O)$_2$]	8	Bicapped trigonal prism	8,9	2.24	2.76	2.50
5	$[NH_4]_4$[Bi(nta)$_2$(NCS)]	9	Tricapped trigonal prism	9	2.36	2.55	2.60–2.71
6	$[CN_3H_6]$[Bi(edta)(H_2O)]	8	Square antiprism	12	2.34	2.70	2.56–2.59
7	Bi(Hedta)	8	Square antiprism	11	2.40	2.62	2.46
8	$[NH_4]$[Bi(edta)]·H_2O	8	Bicapped octahedron	11	2.29	2.80	2.48–2.49
9	Bi(Hedta)·$2H_2O$	8	Bicapped trigonal prism	8	2.29	2.68	2.46–2.58
10	K[Bi(Hdtpa)(H_2O)]·$4H_2O$	9	Monocapped square antiprism	13	2.36	2.75	2.49, 2.55, 2.67
11	$[CN_3H_6]_2$[Bi(dtpa)]·$4H_2O$	9	Monocapped square antiprism	8	2.37	2.69	2.54, 2.64, 2.67



(a)

(b)

Fig. 5 Co-ordination polyhedra around (*a*) Bi(1) and (*b*) Bi(2) in compound **2**[17]

square faces requires the involvement of two or one bridging oxygen, respectively; in the dtpa complex **10** the same is achieved by the presence of a co-ordinating water molecule. In compound **1** the ttha ligand is self-sufficient as regards the complete co-ordination (Fig. 6). A quite different situation was found in ttha complexes described previously with Cr^{III},[20] Sb^{III},[21] Cu^{II}[22] and V^{IV} (vanadyl);[23] all these compounds appear as dinuclear species in which the ttha ligand symmetrically chelates the two metal atoms using two nitrogens and three oxygens.

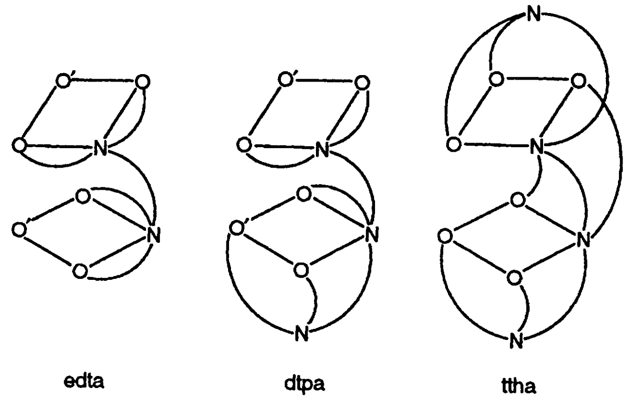


Fig. 6 Comparison of the co-ordination modes in polyaminocarboxylate complexes of Bi^{III} with edta, dtpa and ttha

In both compounds **1** and **2** as in all the analogous bismuth complexes described so far, the Bi–O bonding distances vary within a wide range. In **1** the shortest Bi–O bond lengths (2.32 Å) are comparable with the mean values observed for the shortest bonds in compounds **3**–**11**. The longest Bi–O distances (2.99–3.05 Å) are however significantly larger than in those compounds, but the oxygen atoms involved in these bonds are not of the same nature. If one excepts the case of the nta complexes in which two ligand molecules are involved in co-ordination (compounds **3** and **5**), these values lie in the range 2.60–2.80 Å, but correspond to interactions between Bi atoms and oxygen atoms belonging either to water molecules or to bridging acetate groups. In **1** there are no acetate groups in bridging positions. A further difference concerns the Bi–N distances, the maximum value (2.81 Å) of which is here much larger than the common values. In **2** the minimum Bi–O bond lengths and the average Bi–N distances are comparable with those in **3**–**11**, the only difference being observed in one of the longest Bi–O bond lengths (2.92 Å), which is again larger than the common values. Bismuth–oxygen bond lengths larger than 3.0 Å were previously observed in the citrate complex NH_4[Bi(cit)]·$2H_2O$,[24] as the result of the stereochemical activity of the bismuth lone pair. Such an effect is definitely not present in compounds **1** and **2**.

The Bi ··· Bi contact distances observed in these compounds are rather large (> 4.7 Å in **2**) and consistent with the absence of any interaction. In each acetate group of compounds **1** and **2**, the C′–O bonds involving the co-ordinated oxygens are eclipsed by the C–N bond (torsion angles N–C–C′–O between 4 and 19° in **1**, −6 and −27° in **2**). In the cydta complex **2** the chair conformation of the ligand is not altered by the chelation process.

Without discussing the choice of appropriate reference values for the Bi–N or the Bi–O distances,[8] calculations of the so-called 'valence bond sum'[25] for the Bi atoms in both complexes are consistent with the tervalent state of the central atom.

Acknowledgements

The authors acknowledge the Belgian National Fund for Scientific Research (F.N.R.S.), Brussels and the Catholic University of Louvain (FDS) for financial support.

References

1 A. J. Wagstaff, P. Benfield and J. P. Monk, *Drugs*, 1988, **36**, 132.
2 H. Maeda, T. Tanaka, M. Fukutomi and T. Asano, *Jpn. J. Appl. Phys.*, 1988, **27**, L209.
3 T. Fujisawa, A. Takagi, T. Honjoh, K. Okuyama, S. Ohshima, K. Matsuki and K. Muraishi, *Jpn. J. Appl. Phys.*, 1989, **28**, 1358.
4 C. T. Chu and B. Dunn, *J. Am. Ceram. Soc.*, 1987, **70**, C-375.
5 N. H. Wang, C. M. Wang, H. C. I. Kao, D. C. Ling, H. C. Ku and K. H. Lu, *Jpn. J. Appl. Phys.*, 1989, **28**, L1505.
6 P. Courty, H. Ajot, C. Marcilly and B. Delmon, *Powder Technol.*, 1973, **7**, 21.
7 D. Beltran-Porter, E. Martinez-Tamayo, R. Ibanez, A. Beltran-Porter, J. V. Folgado, E. Escriva, V. Munoz, A. Segura and A. Cantarero, *Mater. Res. Bull.*, 1988, **23**, 987.
8 S. P. Summers, K. A. Abboud, S. R. Farrah and G. J. Palenik, *Inorg. Chem.*, 1994, **33**, 88.
9 K. D. Suyarov, L. M. Shkol'nikova, R. L. Davidovich and V. S. Fundamenskii, *Koord. Khim.*, 1991, **17**, 455.
10 K. D. Suyarov, L. M. Shkol'nikova, M. A. Porai-Koshits, V. S. Fundamenskii and R. L. Davidovich, *Dokl. Akad. Nauk SSSR*, 1990, **311**, 1397.
11 L. M. Shkol'nikova, K. D. Suyarov, R. L. Davidovich, V. S. Fundamenskii and N. M. Dyatlova, *Koord. Khim.*, 1991, **17**, 253.
12 R. N. Shchelokov, Y. N. Mikhailov, V. E. Mistryukov and A. V. Sergeev, *Dokl. Akad. Nauk SSSR*, 1987, **293**, 642.
13 A. B. Ilyukhin, L. M. Shkol'nikova, R. L. Davidovich and I. N. Samsonova, *Koord. Khim.*, 1991, **17**, 903.
14 G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, 1986.
15 G. M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, 1993.
16 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
17 W. D. S. Motherwell and W. Clegg, PLUTO, Program for plotting molecular and crystal structures, University of Cambridge, 1978.
18 L. M. Shkol'nikova, G. V. Ployanchuk, N. M. Dyatlova, M. A. Porai-Koshits and V. G. Yashunskii, *Zh. Strukt. Chem.*, 1983, **24**, 92.
19 R. D. Rogers, A. H. Bond and S. Aguinaga, *J. Am. Chem. Soc.*, 1992, **114**, 2960.
20 G. D. Fallon and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, 1974, **30**, 1987.
21 H. Sheng-Zhi and X. Zhao-Xiong, *Jiegou Huaxue* (*J. Struct. Chem.*), 1991, **10**, 81.
22 P. Leverett, *J. Chem. Soc., Chem. Commun.*, 1974, 161.
23 G. D. Fallon and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, 1976, **32**, 71.
24 W. A. Herrmann, E. Herdtweck and L. Pajdla, *Z. Kristallogr.*, 1992, **198**, 257.
25 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.

Received 11th December 1995; *Paper* 5/08040A