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Review

Bismuth(III) complexes with aminopolycarboxylate and polyaminopolycarboxylate ligands: Chemistry and structure

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Contents

Abstract

This review concerns data on the chemistry and structures of bismuth(III) complexes with aminopolycarboxylate (APC) and polyaminopolycarboxylate (PAPC) ligands. In aqueous solutions Bi(III) binds strongly to both APC and PAPC ligands. Recently these ligands have been considered for bismuth radioisotope chelation in regards to their use in nuclear medicine. The solid state structures of Bi(III) coordination compounds with APC and PAPC ligands are governed mainly by three considerations: (i) low-dentate ligands lead to strong interactions between Bi atoms and donor atoms on the neighboring complexes which often produce oligomeric and polymeric structures; (ii) increasing the number of donor atoms

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in the ligands and the presence of additional ligands in the coordination sphere of Bi atom leads preferentially to monomeric structures; (iii) the presence of bridging carboxylate groups leads to different nuclearities, from dimers to infinite structures. Several aspects of recent applications of Bi(III) APC and PAPC complexes are also discussed.

Keywords: Bismuth(III); Complexes; Aminopolycarboxylate ligands; Polyaminopolycarboxylate ligands; Crystal structure

1. Introduction

Compounds of Bi(III) have received increased interest recently due to their multiple applications in diverse areas including medicine [1], materials [2], organic synthesis [3], and catalysis [4]. Even though bismuth is a p-block element, it is one of the more metallic of that part of the periodic table and forms stable complexes with aminopolycarboxylate (APC) and polyaminopolycarboxylate (PAPC) ligands [5]. In this review, the Bi(III) complexes with APC and PAPC ligands are systematized by the number of nitrogen atoms of the ligands in mono-, di- and polyaminopolycarboxylates.

According to Pearson's hard–soft acid–base theory [6], Bi(III) is a borderline metal ion, but it has a high affinity for multidentate ligands containing O and N donor atoms [7]. Hence, anions of aminopolycarboxylic and polyaminopolycarboxylic acids are highly versatile ligands towards Bi(III). The stability constants of these Bi(III) APC and PAPC complexes are usually very high: e.g. K_{BiL} of Bi(edta)$^-$ was reported in [8] to be 26.7, while that of Bi(dota)$^-$ reaches an even higher value of 30.3 [9]. As result, these complexes are stable and can be isolated even at low pH. Although Bi(III) has a strong tendency to hydrolyze, in the presence of these strongly chelating ligands it is stabilized up to pH 10 [8]. Table 1 summarizes selected stability constants for some Bi(III) complexes with APC and PAPC ligands.

Increasing the number of donor atoms of the ligands and the number of chelating rings formed usually results in higher stability of the complexes. The data presented in Table 1 shows, however, that the denticity of the ligands is only one of the factors determining the stability of Bi(III) APC and PAPC complexes in aqueous solution. The high number of donor atoms of the ligands and of chelating rings are not always reflected in high values of the stability constants; other factors that should be considered are the charge of the ligand, the preorganization, and the steric efficiency in which the ligand surrounds the Bi(III) ion to form a cage-like structure. A significant increase in complex stability is observed in Bi(III)–cdta compared to Bi(III)–edta complex. The cyclohexyl moiety leads to a conformation in which the donor atoms are held in optimized positions for complex formation. As a result, a four order increase in the stability constant is observed.

Table 1
Selected stability constants for some 1:1 Bi(III) complexes with APC and PAPC ligands arranged in a general order of increasing denticity of the ligand

Complex	*T* (K)	log *K*	References
Bi–ida	298	12.94	[10]
Bi–heida	298	14.82	[11]
Bi–nta	293	18.2	[12]
Bi–hedta	293	22.3	[12]
Bi–egta	293	23.8	[12]
Bi–edta	293	27.8	[12]
Bi–cdta	298	31.9	[13]
Bi–do3a–Bu	298	26.8	[9]
Bi–dota	298	30.3	[9]
Bi–dtpa	293	30.7	[12]
Bi–ttha	298	22.59	[14]

By virtue of their high thermodynamic stability, Bi(III) APC and PAPC complexes have been extensively used in analytical chemistry for complexometric titrations [15–17]. Since some of these complexes are stable even at low pH (as low as 0.5–1.0), bismuth can be determined without any interference in the presence of many other metals. For instance, a mixture containing Bi(III), Cd(II) and Ca(II) can be analyzed with a standard Na_2H_2edta solution by titrating Bi(III) at pH 1–2, followed by the titration of Cd(II) at pH 4, and finally Ca(II) at pH 8 [15].

The large Bi(III) ion (1.03 Å for CN 6 and 1.17 Å for CN 8 [18]) forms 1:1 or 1:2 complexes with APC and PAPC ligands and exhibits coordination numbers between 7 and 10. However the octa-coordination of Bi(III) is by far the most frequent (59 out of 69) among the structures. Bismuth(III) complexes with APC and PAPC ligands are obtained easily by reaction of Bi(III) oxide, hydroxide or oxocarbonate with the corresponding acids, usually at reflux in water. Complexes of Bi(III) with few donor atoms generally exhibit low solubility. By increasing the number of donor atoms on the ligands, the corresponding Bi(III) complexes usually display higher solubility, facilitating their crystallization.

Briand and Burford [7] briefly mentioned some recent work on Bi(III) APC and PAPC complexes, while the recent Comprehensive Coordination Chemistry II [19] devoted several pages to these compounds. Hassfjell and Brechbiel [20] also provided data concerning the chelation of Bi(III) by some PAPC ligands, but only in the context of their application as carrier molecules for $^{212/213}$Bi in cancer therapy. Given their broader scope, these contributions generally do not discuss details. It is our aim in the present work to concentrate on the chemistry, properties and crystal structure of Bi(III) aminopolycarboxylates and polyaminopolycarboxylates, especially emphasizing the dependence of these properties on the nature of the chelate, supplementary ligands, and outer-sphere cations. We also set out to establish the various ligand bonding modes that are involved in coordination to Bi(III). Another goal is to bring into focus the rapidly growing area of applications of these complexes.

The increasing interest in Bi(III) APC and PAPC complexes has ensued as a result of a variety of factors:

(i) bismuth(III) complexes with aminopolycarboxylate and polyaminopolycarboxylate ligands have found many applications in analytical chemistry, including complexometric titrations;

(ii) ^{212}Bi and ^{213}Bi radioisotopes are among the most promising candidates for radioimmunotherapy. Medical chelation therapy requires chelate ligands forming radiometal complexes of high stability *in vivo* for the period of time the agent is in the body;

(iii) APC and PAPC ligands are used as chelate agents in different processes for preparation of metallic bismuth nanoparticles, and other high-tech materials, such as bismuth oxide or chalcogenide materials;

(iv) bismuth(III) heterometallic APC and PAPC complexes are attractive as single-source molecular precursors to mixed oxide systems with promising properties.

For some of these applications all that is necessary is an APC or PAPC ligand that will bind Bi(III) strongly to form highly stabilized structures; however, for biomedical applications, other factors, such as kinetic inertness and biocompatibility play an important role, too. Another important factor is the structure of the complex. For instance, involving water or other additional ligands in the coordination sphere, as well as the formation of polynuclear species could influence the utility of the specific complexes.

Since the number of investigated Bi(III) APC and PAPC complexes has substantially increased over the recent years, this work will try to give a comprehensive and comparative review on this subject. The sections of the review are organized according to the number of amine nitrogen donor atoms present in the ligand (mono-, di- or polyaminopolycarboxylates). The tables at the end of the corresponding sections summarize the most important structural features of these complexes (e.g. CN, polyhedra, bond distances, geometry, nuclearity, etc.).

2. Bismuth(III) complexes with monoaminopolycarboxylate ligands

2.1. Bi(III) complexes with iminodiacetate ligands

Bismuth(III) in solution and in the solid state forms stable complexes with anions of iminodiacetic acid. The complexation of Bi(III) with ida^{2-} has been studied spectrophotometrically [10]. In the pH range 0.6–2 the formation of a 1:1 Bi–ida complex was proposed. However in solid state only the 1:2 complex was isolated, namely Bi(Hida)(ida) [21], which has a poor solubility in water (0.2 g in 100 g of H_2O at 90 °C). The compound can be recrystallized from its aqueous solutions, which are slightly acidic (pH 5). Bi(Hida)(ida) proved to be stable in air and does not lose weight upon heating to 200 °C. At 220 °C the complex starts to decompose, giving rise ultimately to Bi_2O_3 by 480 °C. IR spectroscopic data suggest a polymeric structure of Bi(Hida)(ida), involving Bi–O bridging bonds [21]. The X-ray structure determination of Bi(Hida)(ida) [22] confirmed the IR data.

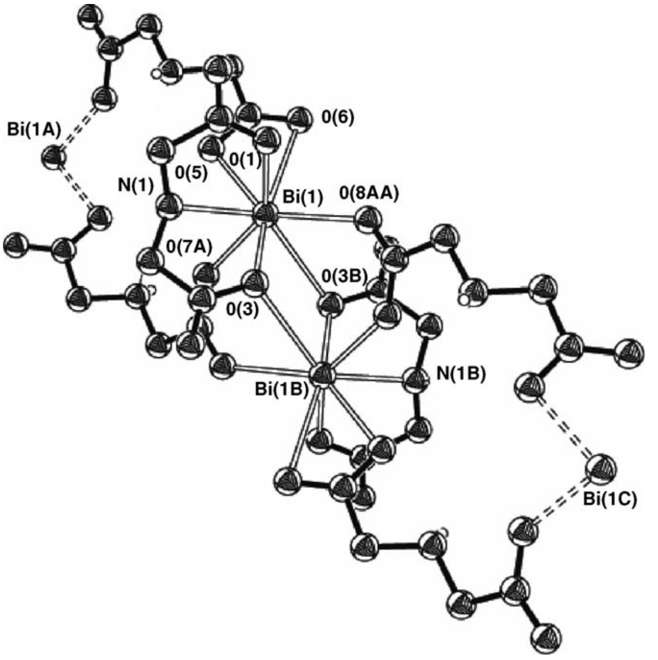


Fig. 1. ADE representation of a fragment of the polymeric ribbon in [Bi(Hida)(ida)].

In the polymeric chain structure of [Bi(Hida)(ida)] each Bi atom is coordinated by one N atom and two carboxylate O atoms of the ida^{2-}–ligand, four O donor atoms of the $Hida^{-}$ bridging ligands, each of them being also coordinated to three other bismuth atoms (Fig. 1). Additionally, Bi(III) forms a bridging bond with the O atom of ida^{2-}-ligand of the neighbor unit. Bi(III) has a distorted octa-coordinate environment. The bond distances Bi–$O_{carboxylate}$ (ida^{2-}) are relatively short (2.236(2) and 2.296(2) Å), while Bi–$O_{carboxylate}$ ($Hida^{-}$) are much longer, within the range 2.405(2)–2.825(2) Å (Table 2). The Bi(III)–O contact (ida^{2-}) to the neighboring unit is 2.854(2) Å. Interestingly, there is only one structure, other than Bi(Hida)(ida), where $Hida^{-}$ and ida^{2-} coordinate at the same time to a metal ion—$[Pr_2(H_2O)_4(Hida)_2(ida)]Cl_2\cdot 3H_2O$ [23].

2.2. Bi(III) complexes with nitrilotriacetate ligands

Complexation of Bi(III) with anions of H_3nta in solution has been investigated by several different methods. Potentiometric titration of Bi(III) with H_3nta in aqueous solution showed that two types of complexes are formed, but no stability constants were determined [24]. Reaction of bismuth(III) perchlorate and H_3nta has been monitored by means of UV spectroscopy [25]. The formation constants of both 1:1 and 1:2 complexes have been determined ($\log \beta = 17.53 \pm 0.06$ and 26.56 ± 0.07, respectively). The stability constant of the 1:1 complex, as determined by polarography (17.55 ± 0.34) [26], was found to be in good agreement with the previously reported values. Ershova et al. [27] studied the interaction of $[BiCl_6]^{3-}$ with nitrilotriacetic acid by potentiometry in a large pH range. The formation constants of the mixed ligand complex $[Bi(Hnta)_2Cl_2]^{3-}$ and a deprotonated $[Bi(nta)_2]^{3-}$ complex were reported to be 14.9 and 27.6.

Both 1:1 and 1:2 Bi(III)–nta complexes have been isolated in solid state. $Bi(nta)\cdot 2H_2O$ was obtained by interaction of equimolar quantities of $Bi(OH)_3$ and H_3nta [28] and by reaction of $(BiO)_2CO_3$ and H_3nta [29]. Complexes of the general

Table 2
Structural features of bismuth(III) monoaminopolycarboxylates

Compound	CN, polyhedron	Type of structure	Bond distances (Å)		References
			d(Bi–N)	*d*(Bi–O)	
[Bi(Hida)(ida)]	8, Distorted	Polymeric (ribbon)	2.382(2)	2.236(2), 2.296(2), 2.405(2), 2.425(2), 2.652(2), 2.825(2)[a], 2.854(2)[a]	[22]
$[Bi(nta)(H_2O)_2]$	8, BTP	Polymeric (ribbon)	2.500(8)	2.253(7); 2.258(6), 2.501(6), 2.665(6)[a], 2.435(6)[b], 2.403(6)[c], 2.767(9)[c]	[29]
$[Bi(nta)(H_2O)_2]$	8, BTP	Polymeric (ribbon)	2.498(8)	2.242(7); 2.251(8), 2.517(6), 2.659(6)[a], 2.540(6)[b], 2.415(8)[c], 2.759(9)[c]	[32]
$(NH_4)_3[Bi(nta)_2]$	8, BTP	Monomeric	2.58(1), 2.60(2)	2.40(1) × 3, 2.44(1) × 3	[33]
$(NH_4)_3[Bi(nta)_2]$	8, Cube	Monomeric	2.60 × 2	2.42 × 6	[34]
$K_3[Bi(nta)_2]$	8, Cube	Monomeric	2.592(5) × 2	2.435(3) × 6	[31]
$K_3[Bi(nta)_2]\cdot 2H_2O$	8, Cube	Monomeric	2.600(3) × 2	2.418(3) × 2, 2.480(3) × 2, 2.496(3) × 2	[35]
$(CH_6N_3)_3[Bi(nta)_2]\cdot 0.5(CH_6N_3)(HCO_3)\cdot 3H_2O$	8, Cube	Monomeric	2.634(1) × 2	2.421(1) × 2, 2.446(1) × 2, 2.460(1) × 2	[36]
$(NH_4)_4[Bi(nta)_2(NCS)]\cdot H_2O$	9, TTP	Monomeric	2.605(4) × 2, 2.71(1) (NCS)	2.363(4) × x2, 2.541(4) × 2, 2.551(5) × 2	[32]
$K_2[Bi(nta)(Hnta)]\cdot H_2O$	10 (7 + 3), No data	Polymeric (layer)	2.496(5)	2.448(4) × 3, 2.589(4) × 3, 2.781(5)[b] × 3	[38]
$[Bi(heida)(H_2O)]\cdot H_2O$	8, BTP	Polymeric (layer)	2.49(2)	2.14(1), 2.33(1), 2.34(1), 2.46(1)[a], 2.98(1)[a], 2.70(2)[b], 2.77(2)[c]	[44]
$NH_4[Bi(Hheida)_2]\cdot 3H_2O$	8, D	Monomeric	2.549(5), 2.599(4)	2.355(3), 2.369(4), 2.440(3), 2.522(3), 2.723(4), 2.731(3)	[46]
$K[Bi(Hheida)_2]\cdot 3H_2O$	8, D	Monomeric	2.547(5), 2.615(5)	2.260(4), 2.351(4), 2.374(4), 2.450(4), 2.746(5), 2.779(4)	[31]
$(CH_6N_3)_2[Bi(Hheida)(heida)]\cdot 3H_2O$	8, D	Monomeric	2.561(9), 2.582(9)	2.109(7), 2.354(7), 2.414(7), 2.447(7), 2.785(7), 2.817(9)	[46]
$[Bi(2,6\text{-}Hpydc)(2,6\text{-}pydc)(DMSO)]_2$	8, No data	Dimeric	2.418(9), 2.481(9)	2.209(8), 2.342(7), 2.507(6), 2.578(6)[a], 2.613(8) (DMSO), 2.736(8)	[48]
$[pydaH]_2[Bi_2(pydc)_4(H_2O)_2]\cdot 4H_2O$	8, No data	Dimeric	2.435(3), 2.555(3)	2.327(3), 2.422(3), 2.423(3), 2.588(3), 2.589(3)[c], 2.678(3)[a]	[50]

[a] Bridging Bi–O(carboxylate).
[b] Bridging Bi–O(carbonylic).
[c] $Bi–O(H_2O)$.

formula $M_3[Bi(nta)_2]\cdot nH_2O$ ($M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+, $NH_4{}^+$, and guanidinium $CH_6N_3{}^+$) were isolated by dissolution of equimolar quantities of $Bi(OH)_3$ and H_3nta, and addition of MOH to achieve pH 5 [28]. Complexes $M_2[Bi(nta)(Hnta)]\cdot H_2O$ ($M^+ = K^+$, $NH_4{}^+$), containing both nta and Hnta ligands have also been obtained [30]. These complexes proved to be isostructural. Examples of other mixed-ligand Bi(III)–nta complexes include Bi(nta)·3tu [28] and $(NH_4)_4[Bi(nta)_2(NCS)]\cdot H_2O$ [28].

Asato et al. [31] studied the solution behavior of the $[Bi(nta)_2]^{3-}$ species by means of ^1H and ^{13}C NMR and proved that these are very stable over the pH* range 4.0–9.0 (pH* is the pH in D_2O). The chemical shift of the CH_2 groups is constant ($\delta = 3.924$ ppm) in the interval of pH* 4.0–9.0, proving the existence of one type of $[Bi(nta)_2]^{3-}$ complex in solution. The ^{13}C NMR spectra show one set of resonances from the ligand in $[Bi(nta)_2]^{3-}$: 182.4 ppm for the COO^- and 64.9 ppm for the CH_2 groups, confirming the formation of a single $[Bi(nta)_2]^{3-}$ complex in solution. At pH* > 9, a slight up-field shift is noted, probably due to hydrolysis, with the formation at pH* > 11 of an amorphous white precipitate. At pH* < 4.0 peak broadening and a down-field shift is observed. The authors explained these observations by protonation of carboxylate groups and release of nta^{3-} ligands from the coordination sphere of the complex and a very rapid ligand exchange process between coordinated and free ligands.

The reported crystal structures of bismuth(III) nitrilotriacetates include: $[Bi(nta)(H_2O)_2]$ [29,32], $(NH_4)_3[Bi(nta)_2]$ [33,34], $K_3[Bi(nta)_2]$ [31], $K_3[Bi(nta)_2]\cdot 2H_2O$ [35], $(CH_6N_3)_3[Bi(nta)_2]\cdot 0.5(CH_6N_3)(HCO_3)\cdot 3H_2O$ [36], $[Bi_xTb_{1-x}(nta)(H_2O)_2]_n$ [37], $K_2[Bi(nta)(Hnta)]\cdot 2H_2O$ [38], and $(NH_4)_4[Bi(nta)_2(NCS)]\cdot H_2O$ [29].

IR investigation of $[Bi(nta)(H_2O)_2]$ [28] showed that nta^{3-} is present as a tetradentate ligand, and the water molecules are coordinated to Bi(III). IR data suggested a polymeric structure, involving bridging carboxylate groups. X-ray structure investigation [29,32] confirmed the polymeric motif in this complex (Fig. 2). The nta^{3-} ligand exhibits a

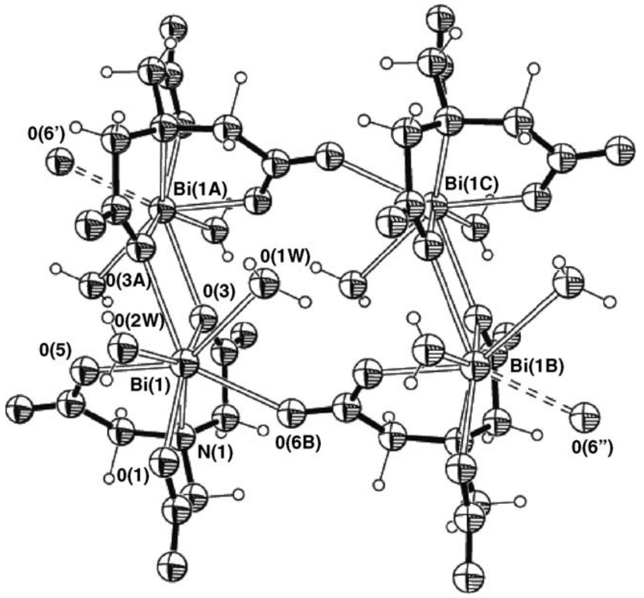


Fig. 2. ADE drawing of a fragment of the polymeric ribbon in [Bi(nta)(H_2O)$_2$].

tetradentate–chelate (N + 3O) and double-bridging (2O) function. The coordination environment of the Bi atom includes one N atom, three carboxylate oxygen atoms, two O atoms of water molecules, and two bridging oxygen atoms of the neighboring complexes. Interestingly, one water molecule is bound more strongly (Bi–O(1W) = 2.415(8) Å), than the second (Bi–O(2W) = 2.759(9) Å).

Crystals of (NH_4)$_3$[Bi(nta)$_2$] [33] exhibit trigonal symmetry. The structure was initially solved within space group R3 with two crystallographically independent nta^{3-} ligands. The coordination polyhedron of the Bi atom was initially described as a bicapped trigonal prism with the capped atoms at the triangular faces, that was quite unexpected. Later, the crystal structure of an isostructural complex Tl^{I}_3[Tl^{III}(nta)$_2$] was determined and the authors [34] solved it within the space group $R\bar{3}$, the coordination polyhedron being a cube. Based on the fact that the proposed model [33] for the structure of (NH_4)$_3$[Bi(nta)$_2$] was partially correct, the authors of [34] recalculated the coordinates of the atoms considering the real space group to be $R\bar{3}$, and finally obtained a more realistic model with the coordination polyhedron of Bi(III) also being a cube.

The corresponding potassium salt, K_3[Bi(nta)$_2$] was obtained by reaction of [Bi(nta)(H_2O)$_2$] with K_3nta in aqueous solution with subsequent addition of methanol to achieve the crystallization [31]. The complex is isostructural with (NH_4)$_3$[Bi(nta)$_2$] and contains two equivalent nta^{3-} ligands, exhibiting a tetradentate–chelate coordination (N + 3O). The authors [31] described the coordination polyhedron as a dodecahedron but, as in the case of (NH_4)$_3$[Bi(nta)$_2$], it is better described as a slightly distorted cube. The potassium cations connect the monomeric anions in a 3D network.

The coordination polyhedron around the Bi(III) center in the structure of the dihydrate, K_3[Bi(nta)$_2$]·2H_2O [35] is a cube, but significantly distorted. In contrast to the crystal structures of (NH_4)$_3$[Bi(nta)$_2$] and K_3[Bi(nta)$_2$] where all Bi–O distances are equal, in the structure of K_3[Bi(nta)$_2$]·2H_2O, the Bi–O bonds have different lengths (2.418(3), 2.480(3) and 2.496(3) Å). The two types of crystallographically independent K^+ cations and [Bi(nta)$_2$]$^{3-}$ anions are connected in a 3D framework by hydrogen bonds.

Addition of guanidinium carbonate to a solution obtained by dissolution of bismuth hydroxide and nitrilotriacetic acid in water at reflux up to pH 5–6 resulted in the formation of (CH_6N_3)$_3$[Bi(nta)$_2$]·0.5(CH_6N_3)(HCO_3)·3H_2O [36]. The [Bi(nta)$_2$]$^{3-}$ anion contains Bi(III) in a distorted cubic environment formed by two tetradentate (N + 3O) nta^{3-} ligands. In the coordination polyhedron the angle between nitrogen donors of the two ligands and corresponding oxygen donors is close to 180°. The Bi–O bond distances are in the range of 2.421(1)–2.460(1) Å, while the Bi–N bond distance is 2.634(1) Å, slightly longer than in other bismuth(III) nitrilotriacetate complexes.

A heterobinuclear nitrilotriacetate complex, [Bi_xTb_{1-x}(nta)(H_2O)$_2$]$_n$, was obtained by reaction of aqueous (NH_4)$_3$[Bi(nta)$_2$] and Tb(NO_3)$_3$ [37]. There is a statistical occupational disorder in the polymeric structure of the complex with an approximate ratio of bismuth to terbium of 7:3. The metal ions (CN 8) are coordinated by four (N + 3O) donor atoms of nta^{3-} ligand, oxygen atoms of the two water molecules and two carboxylate oxygen atoms of neighboring molecules. The metal–nitrogen bond distance is 2.528(7) Å, while the metal–oxygen bond distances in the complex range from 2.238(6) to 2.697(7) Å. The shortest of the Bi–O bonds are associated with non-bridging oxygen atoms of the nitrilotriacetate ligand (2.265(6) and 2.238(6) Å, respectively). By contrast, the bond distance between the metal and the third oxygen of the same nta ligand is longer (2.502(6) Å) due to the fact that it bridges to another complex to form a four-membered Bi_2O_2 ring.

The reaction of [Bi(nta)(H_2O)$_2$], H_3nta and KOH at pH 5 results in formation of K_2[Bi(nta)(Hnta)]·H_2O [38]. In the crystal structure of this mixed ligand complex the H atom in the Hnta^{2-} ligand is localized on the N atom. The Bi atom is coordinated by the nta^{3-} ligand in a tetradentate–chelate mode and by three betaine Hnta^{2-} ligands. In its turn, each Hnta^{2-} ligand represents a hexadentate bridge between three bismuth atoms. The CN of the Bi atom in K_2[Bi(nta)(Hnta)]·H_2O is equal to 7 + 3. It is interesting to note that in the crystal structure of Cs[Sn(nta)(Hnta)]·H_2O [38] the hydrogen atom of the Hnta^{2-} ligand is situated on one free acetate group, the nitrogen atom being coordinated to Sn(IV). Two different types of protonation for the Hnta^{2-} ligands can be explained by the nature of the complexing agent. The metal ions that form ionic bonds with the nitrogen atom contribute to preservation of the betaine structure of Hnta^{2-}, while metal ions with strong affinity to nitrogen contribute proton transfer from Hnta^{2-} to one of the carboxylate groups.

When the reaction of Bi(OH)$_3$:H_3nta (ratio 1:2) and ammonia is performed in the presence of NH_4NCS, (NH_4)$_4$[Bi(nta)$_2$(NCS)]·H_2O is obtained. The crystal structure of this mixed-ligand complex [32] is formed by $NH_4{}^+$ cations [Bi(nta)$_2$(NCS)]$^{4-}$ complex anions and H_2O molecules. In the [Bi(nta)$_2$(NCS)]$^{4-}$ anions (Fig. 3), the two nta^{3-} ligands exhibit

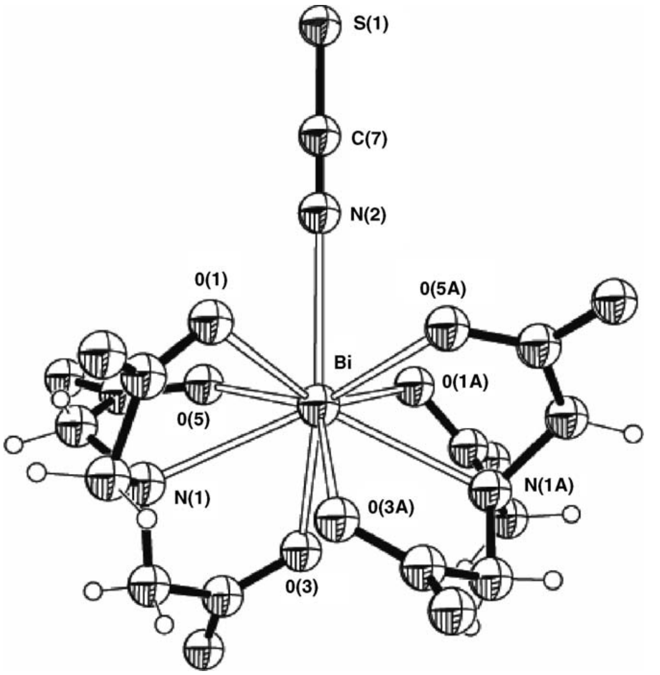


Fig. 3. ADE drawing of the complex anion $[Bi(nta)_2(NCS)]^{4-}$ in $(NH_4)_4[Bi(nta)_2(NCS)]\cdot H_2O$.

a tetradentate–chelate mode (N + 3O), each using the N donor atom and three O atoms of the acetate groups. The NCS-ligand is involved in coordination to the Bi atom through the N atom (Bi–N 2.71(1) Å), which is close to the Bi–N bond lengths in $Rb[Bi(NCS)_4]$ [39].

2.3. *Bi(III) complexes with 2-hydroxyethyliminodiacetate ligands*

The reaction of Bi^{3+} with anions of H_3heida has been investigated by means of spectrophotometry and shows a 1:1 stoichiometry of the complex with the formation constant equal to 14.82 ± 0.03 [11]. The same value for the stability constant was reported in [40]. The reaction of $[BiCl_6]^{3-}$ with equimolar amounts of H_3heida was studied by means of potentiometry [41]. It was established that at pH 2.2–3.48 no complexation occurs, while at pH > 3.48 the precipitation of BiOCl was observed. Interaction of $[BiCl_6]^{3-}$ with excess H_3heida, however, led to the formation of both 1:1 and 1:2 complexes. The stability constants of $[Bi(H_2heida)(Hheida)Cl_2]^{2-}$ and $[Bi(Hheida)_2]^{-}$ are reported to be 18.7 (pH 2.0–4.5) and 24.3 (pH 6.0–9.0).

The pH dependence of ^1H NMR chemical shifts in the Bi(III)–heida system was reported [31]. Equimolar solutions of $Bi(NO_3)_3\cdot 5H_2O$ and H_3heida in D_2O exhibit a pH^* 0.90 (pH in D_2O). The methylene protons of the carboxylate groups show a singlet at 4.47 ppm in the ^1H NMR spectra in D_2O. At pH 1.15, the singlet changes to an AB pattern signal. This suggests coordination of the amine nitrogen at pH 1.15, because the chelation of Bi(III) by N and two carboxylate oxygen atoms gives rise to a magnetic inequivalence of methylene hydrogen atoms. It seems that at pH 1.15 $[Bi(H_2heida)]^{2+}$ is the main species. At pH 1.50, precipitation of $[Bi(heida)(H_2O)]\cdot H_2O$ occurs. Interestingly, at pH 2.0 no signals in the ^1H NMR spectra were detected in solution, showing that all the ligand was precipitated as $[Bi(heida)(H_2O)]\cdot H_2O$, and reflecting the deprotonation of the hydroxyethyl group at pH^* 1.5–2.0. Surprisingly the solubility increases at $pH^* > 9.0$, but no AB pattern signals were found. The authors explained this observation by possible formation of water-soluble oligomeric complexes.

In contrast to the 1:1 system, the 1:2 Bi–heida complex is stable over a wider pH range and was found to be composed of $[Bi(Hheida)_2]^{-}$ species over the pH^* range 2.5–5.5. This fact was confirmed by an invariable ^1H NMR spectrum and by ESI-MS. Above pH 10, the chemical shifts of the coordinating ligand are approaching those of the metal-free ligand, while a further increase of pH above 12 results in hydrolytic decomposition giving rise to an amorphous white precipitate. The ligand exchange between coordinated and free $Hheida^{2-}$ at pH^* 5 proved to be fast.

The hydroxyethyl group of the $Hheida^{2-}$-ion can be deprotonated under certain conditions, leading to $heida^{3-}$ ions. The interaction of $Bi(OH)_3$ with H_3heida in aqueous solution for both 1:1 and 1:2 ratios leads to $Bi(heida)\cdot 2H_2O$ [42,43]. It should be noted that this complex is highly soluble in the presence of H_3heida. Reaction of two equivalents of H_3heida with $Bi(OH)_3$ in the presence of some alkali metal, ammonium or guanidinium cations leads to the formation of well-soluble $MBi(Hheida)_2\cdot nH_2O$, where $M^+ = Na^+$ [42], K^+, Rb^+, Cs^+, NH_4^+ or $CH_6N_3^+$ [43], $n = 1$–3, as well as $(CH_6N_3)_2Bi(Hheida)(heida)\cdot 3H_2O$ [43]. $(CH_6N_3)Bi(Hheida)_2\cdot H_2O$ was obtained as a first fraction from the solution, which resulted from dissolution of guanidinium carbonate in a mixture of $Bi(OH)_3$–H_3heida in 1:2 ratio. The second fraction that precipitated from the solution was $(CH_6N_3)_2Bi(Hheida)(heida)\cdot 3H_2O$.

The IR spectrum of $[Bi(heida)(H_2O)]\cdot H_2O$ showed a narrow intense doublet at 1580 and 1592 cm^{-1} with shoulders at 1615 and 1645 cm^{-1} indicative of the nonequivalence of the Bi–O bonds. Like $[Bi(nta)(H_2O)_2]$, it has been assumed that $[Bi(heida)(H_2O)]\cdot H_2O$ exhibits a polymeric chain structure. IR spectra of $MBi(Hheida)_2\cdot nH_2O$ are distinct from the corresponding $M_3[Bi(nta)_2]$ complexes due to two bands in the $\nu_{as}(COO)$ region, while in the case of $M_3[Bi(nta)_2]$, the $\nu_{as}(COO)$ appears as a single intense band at 1600 cm^{-1}. This indicates a high ionic character in the latter case [43].

$[Bi(heida)(H_2O)]\cdot H_2O$ has a polymeric structure [44]. The distorted bicapped trigonal prismatic environment for bismuth involves two O atoms of deprotonated acetate groups, one O atom of the deprotonated hydroxyethyl group, the nitrogen atom, one water molecule O atom, and three carboxylate O atoms of the neighboring complexes. In $[Bi(heida)(H_2O)]\cdot H_2O$ the $heida^{3-}$ ligand exhibits a tetradentate–chelate (N + 3O) and a triply-bridging (3O) function. The Bi polyhedra are united in dimers ($Bi\cdots Bi' = 3.83$ Å) by means of the bridging O atom of the hydroxyethyl group. The dimers are connected in layers ($Bi\cdots Bi'' = 5.14$ Å) by both oxygen atoms of the two acetate groups of the neighboring complexes. The Bi–carboxylate oxygen chelate bonds are slightly shorter (2.33(1) and 2.34(1) Å) than the Bi–O bridging bond (2.46(1) Å); this is responsible for

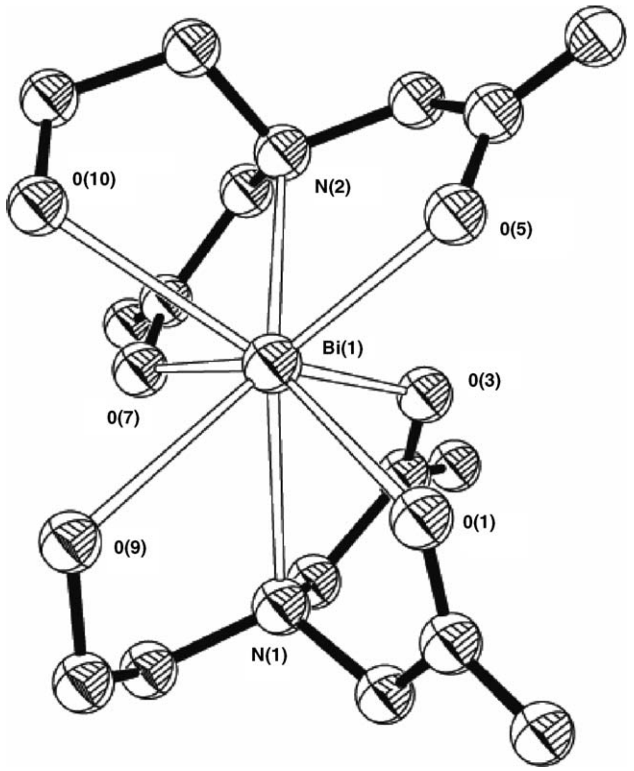


Fig. 4. ADE representation of the complex anion $[Bi(Hheida)_2]^-$ in $NH_4[Bi(Hheida)_2]\cdot 3H_2O$.

formation of the dimers. Meanwhile the bridging Bi–O (2.70(1) and 2.98(1) Å) that connects the layers is longer. The Bi–O (alkoxide) bond distance is very short (2.14(1) Å) and corresponds to a strong Bi–O covalent bond (the sum of covalent radii for Bi and O is 2.16 Å [45]).

Crystal structures of $NH_4[Bi(Hheida)_2]\cdot 3H_2O$ and $(CH_6N_3)_2[Bi(Hheida)(heida)]\cdot 3H_2O$ revealed that both complexes are monomeric [46]. The CN of Bi is 8 in both complexes. In the complex anion $[Bi(Hheida)_2]^-$ (Fig. 4) the central atom is coordinated by the four oxygen atoms of the carboxylate groups, two oxygen atoms of protonated hydroxyethyl groups and two nitrogen atoms. A similar environment for Bi has been observed in $(CH_6N_3)_2[Bi(Hheida)(heida)]\cdot 3H_2O$, the only difference is that one hydroxyethyl group in heida is deprotonated. The coordination polyhedra of the Bi atom in the two complexes can be represented as distorted dodecahedra. The aminocarboxylate ligands in both complexes show a tetradentate–chelate (N + 3O) function. The bond distances of $Bi–O_{hydroxyethyl}$ are slightly longer (2.723(4)–2.817(9) Å) than the Bi–O carboxylate bonds (2.354(7)–2.785(7) Å). In contrast, the Bi–O bond with the deprotonated hydroxyethyl group in the structure of $(CH_6N_3)_2[Bi(Hheida)(heida)]\cdot 3H_2O$ is very short, just 2.109(7) Å and corresponds to a strong covalent bond. So far, this is the shortest chelate Bi–O bond in the structures of reported bismuth complexes with aminopolycarboxylic acids.

The $K[Bi(Hheida)_2]\cdot 3H_2O$ structure was described by Asato et al. [31] and proved to be isostructural with $NH_4[Bi(Hheida)_2]\cdot 3H_2O$ [46].

2.4. Bi(III) complexes with pyridinedicarboxylate ligands

Bismuth(III) complexes with aromatic nitrogen-donor carboxylate ligands include 2,3-, 2,5-, and 2,6-pyridinedicarboxylates. Postel and co-workers [47,48] studied the reaction of Bi_2O_3 and 2,3-, 2,5-, and 2,6-pyridinedicarboxylic acids (H_2L) in aqueous solution and, based on elemental analysis and IR spectra, proposed the same $Bi(HL)_2(OH)$ composition for all three complexes. When Bi_2O_3 is reacted with pyridine-2,6-dicarboxylic acid (H_2pydc) in water at reflux, with subsequent recrystallization of the product from DMSO, a dimeric complex $[Bi(2,6\text{-}Hpydc)(2,6\text{-}pydc)(DMSO)]_2$ is formed. The compound is not soluble in common organic solvents, but is soluble in hot DMF and DMSO. In the dimeric structure of $[Bi(2,6\text{-}Hpydc)(2,6\text{-}pydc)(DMSO)]_2$ (Fig. 5), two bismuth atoms are connected by bridging carboxylic groups of the dipicolinate ions [48]. Each bismuth center is surrounded by four oxygen atoms and two nitrogen atoms of the dipicolinate ions, a bridging oxygen atom from the neighboring complex and one oxygen atom of a DMSO molecule (Bi–O 2.209(8)–2.507(6) Å; Bi–N 2.418(9) and 2.481(9) Å; $Bi–O_{bridging} = 2.577(4)$ Å, $Bi–O_{DMSO}$ 2.613(6) Å).

Reaction of a solution of bismuth(III) subnitrate $Bi_5O(OH)_9(NO_3)_4$ in HCl with pyridine-2,6-dicarboxylic acid in the presence of pyridine-2,6-diamine results in formation of $[\{BiCl(H_2O)(pydc)\}_2]_n$ [49]. The structure of this compound is composed of dimers, linked into an infinite system by means of bridging carboxylate groups. Bismuth has a distorted pentagonal bipyramidal environment, in which the equatorial plane contains the three donor atoms of a $pydc^{2-}$ ligand, the oxygen donor atom of a water molecule and the Bi_2O_2 ring, while the axial sites are occupied by an oxygen atom of the neighboring $pydc^{2-}$ lig-

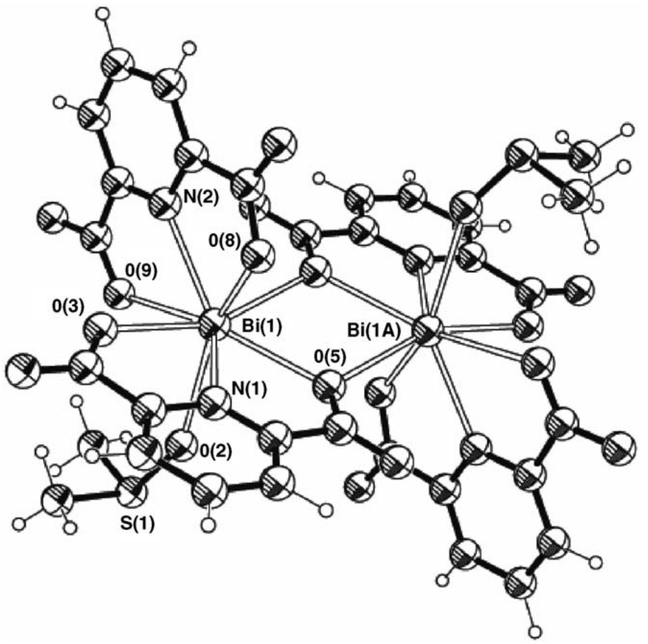


Fig. 5. ADE representation of the dimeric unit in $[Bi(2,6\text{-}Hpydc)(2,6\text{-}pydc)(DMSO)]_2$.

Table 3
Structural features of Bi(III) diaminopolycarboxylates

Compound	CN, polyhedron	Type of structure	Bond distances (Å)		References
			d(Bi–N)	*d*(Bi–O)	
[Bi(Hedta)]	8, SA	Polymeric (layer)	2.465(5) × 2	2.399(3) × 2, 2.472(4) × 2, 2.617(5)[a] × 2	[59]
α-[Bi(Hedta)]$\cdot 2H_2O$	8, SA	Polymeric (layer)	2.43(1), 2.47(1)	2.325(8), 2.329(9), 2.340(9), 2.638(9), 2.78(1)[a], 2.88(1)[a]	[61]
β-[Bi(Hedta)]$\cdot 2H_2O$	8, SA	Polymeric (layer)	2.40(1), 2.575(9)	2.231(8), 2.249(9), 2.403(9), 2.70(1), 2.679(9)[a], 2.697(8)[a]	[60]
β-[Bi(Hedta)]$\cdot 2H_2O$	8, SA	Polymeric (layer)	2.461(8), 2.577(9)	2.295(7), 2.306(9), 2.400(9), 2.642(9), 2.67(1)[a], 2.678(7)[a]	[29]
Li[Bi(edta)] $4H_2O$	7 + 1, No data	Polymeric (layer)	2.432(3), 2.446(3)	2.281(3), 2.339(3), 2.452(3), 2.462(3), 2.866(3)[a], 3.178(3)[a]	[68]
Na[Bi(edta)]$\cdot 3H_2O$	8, SA	Polymeric (layer)	2.491(9), 2.497(8)	2.324(8), 2.331(8), 2.362(8), 2.525(8), 2.637(8)[a], 2.843(8)[a]	[69]
Na[Bi(edta)]$\cdot 3H_2O$	8, SA	Polymeric (layer)	2.495(5), 2.508(5)	2.315(4), 2.336(4), 2.383(5), 2.521(4), 2.636(4)[a], 2.850(7)[a]	[67]
Rb[Bi(edta)]$\cdot 3H_2O$	8, SA	Polymeric (layer)	2.473(2), 2.516(2)	2.293(2), 2.354(2), 2.376(2), 2.571(2), 2.718(2)[a], 2.843(2)[a]	[70]
Cs[Bi(edta)]$\cdot H_2O$	8, SA	Polymeric (zigzag chain)	2.493(2), 2.513(2)	2.302(2), 2.341(2), 2.413(2), 2.599(2), 2.722(3)[a], 2.876(2)[b]	[71]
NH_4[Bi(edta)]$\cdot H_2O$	8, BTP	Polymeric (layer)	2.479(9), 2.49(1)	2.290(9), 2.348(8), 2.473(8), 2.494(8), 2.792(9)[a], 2.805(8)[a]	[59]
$NH_4[Bi_2$(Hedta)(edta)]$\cdot 2H_2O$	8, SA	Polymeric (double chain)	2.464(5), 2.521(5)	2.316(5), 2.319(5), 2.368(5), 2.560(5), 2.752(5)[a], 2.955(5)[b]	[62]
Cs$[Bi_2$(Hedta)(edta)]$\cdot 3H_2O$	8, SA	Polymeric (double chain)	2.451(2), 2.503(2)	2.282(2), 2.341(2), 2.392(2), 2.599(2), 2.774(2)[a], 2.971(2)[b]	[73]
Ca[Bi(edta)]$_2\cdot 9H_2O$	8, SA	Polymeric (chain)	2.460(6), 2.543(6)	2.360(6), 2.367(6), 2.453(6), 2.463(6), 2.778(6)[a], 3.038(7)[b]	[75]
Ba$[Bi_2(edta)_2(H_2O)]\cdot H_2O$	Bi(1) 8, D	Tetrameric	2.47(1), 2.48(2)	2.27(1), 2.33(1), 2.38(1), 2.52(1), 2.78(1)[a], 2.73(1)[c]	[76]
	Bi(2) 8, D	Tetrameric	2.44(1), 2.49(1)	2.26(1), 2.42(1), 2.44(1), 2.47(1), 2.97(1)[a], 2.66(1)[c]	
Co[Bi(edta)]$_2\cdot 9H_2O$	8, SA	Polymeric (chain)	2.427(7), 2.443(6)	2.387(6), 2.402(7), 2.461(7), 2.505(7), 2.732(9)[a], 2.816(7)[b]	[77]
Ni[Bi(edta)]$_2\cdot 9H_2O$	8, SA	Polymeric (chain)	2.437(8), 2.45(1)	2.386(8), 2.400(8), 2.47(1), 2.522(9), 2.73(1)[a], 2.778(9)[b]	[77]
Cu[Bi(edta)]$_2\cdot 9H_2O$	8, SA	Polymeric (chain)	2.442(7), 2.446(9)	2.348(8), 2.375(6), 2.471(7), 2.481(7), 2.710(9)[a], 2.787(6)[b]	[65]
(CH_6N_3)[Bi(edta)(H_2O)]	8, SA	Polymeric (chain)	2.56(1), 2.60(2)	2.35(1), 2.36(2), 2.44(2), 2.46(2), 2.68(1)[c], 2.70(1)[a]	[78,84]
(CH_6N_3)[Bi(edta)(H_2O)]	8, SA	Polymeric (chain)	2.494(4), 2.522(4)	2.352(4), 2.359(4), 2.451(4), 2.452(4), 2.673(4)[c], 2.694(4)[a]	[79]
(CH_7N_4)[Bi(edta)]	8, D	Polymeric (chain)	2.454(4), 2.492(4)	2.296(4), 2.428(4), 2.428(4), 2.435(4), 2.657(4)[b], 2.931(4)[a]	[79]
(enH_2)[Bi(edta)$(H_2O)]_2\cdot 4H_2O$	8, SA	Polymeric (chain)	2.48(1), 2.49(1)	2.291(9), 2.32(1), 2.427(9), 2.476(9), 2.82(1)[a], 2.87(1)[c]	[80]
$(H_3NCH_2CH_2CO_2H)$[Bi(edta)(H_2O)]	8, SA	Dimeric	2.426(7), 2.492(7)	2.315(6), 2.347(6), 2.428(5), 2.601(6), 2.768(6)[b], 2.727(8)[c]	[81]
(CH_6N_3S)[Bi(edta)(H_2O)]	7, No data	Monomeric	2.453(2), 2.487(2)	2.348(2), 2.362(2), 2.391(2), 2.486(2), 2.640(2)[c]	[82]
$[Co(NH_3)_4CO_3]$[Bi(edta)]$\cdot 3H_2O$	8, SA	Polymeric (chain)	2.42(2), 2.51(2)	2.36(1), 2.36(1), 2.50(1), 2.52(2), 2.74(1)[a], 2.79(1)[a]	[83]
$[Co(NH_3)_4C_2O_4]$[Bi(edta)]$\cdot 3H_2O$	8, SA	Polymeric (chain)	2.47(2) 2.49(1)	2.37(1), 2.39(1), 2.43(1), 2.48(2), 2.76(1)[a], 2.76(2)[a]	[84]
Trans-$[Co(NH_3)_4(NO_2)_2]$[Bi(edta)$(H_2O)]\cdot 2H_2O$	8, SA	dimeric	2.495(4), 2.450(4)	2.346(3), 2.413(4), 2.437(4), 2.494(4), 2.670(4)[c], 2.782(4)[a]	[83]
$[Co(NH_3)_2(ala)_2]$[Bi(edta)$(H_2O)]\cdot 5H_2O$	8, SA	Polymeric (chain)	2.47(3) 2.49(3)	2.41(1), 2.41(2), 2.42(2), 2.47(2), 2.68(3)[a], 2.73(3)[c]	[84]
[Co(Hdmg)$_2$(*o*-tol)$_2$][Bi(edta)$(H_2O)]\cdot 5H_2O$	8, SA	Dimeric	2.453(5), 2.500(5)	2.328(5), 2.380(5), 2.466(5), 2.497(4), 2.697(5)[c], 2.812(4)[b]	[86]
[Co(Hchdd)$_2$(*p*-tol)$_2$][Bi(edta)]$\cdot 4H_2O$	8, D	Polymeric (chain)	2.481(3) × 2	2.488(2) × 2, 2.342(2) × 2, 2.705(2)[b] × 2	[87]
[Bi(Hcdta)]$\cdot 5H_2O$	Bi(1) 8, SA	Polymeric (chain)	2.49(1), 2.51(1)	2.286(9), 2.339(9), 2.439(9), 2.58(1), 2.695(9)[a], 2.92(1)[a]	[111]
	Bi(2) 8, SA	Polymeric (chain)	2.50(1), 2.51(1)	2.404(9), 2.43(1), 2.454(8), 2.50(1), 2.612(9)[a], 2.62(1)[a]	
Cs[Bi(cdta)]$\cdot 5.5H_2O$	8, SA	Polymeric (ribbon)	2.482(3) 2.485(3)	2.363(3), 2.399(3), 2.413(3), 2.504(4), 2.712(3)[a], 2.799(4)[b]	[112]
$[Bi_{12}(H_2hpdta)_4(Hhpdta)_6(H_2O)_{12}]\cdot 80H_2O$	9, MSA or TTP	Dodeca-nuclear	2.429(5)-2.633(6)	2.262(5)-2.524(4), 2.522(4)–2.854(5)[b], 2.672(5)–3.080(5)[a], 2.657(5)–3.215(5)[c], 2.187(4)–2.683(5) (alkoxo)	[114]

[a] Bridging Bi–O(carbonylic).

[b] Bridging Bi–O(carboxylate).

[c] Bi–O(H_2O).

and, and by a chlorine atom (Bi–O 2.365(3)–2.633(3) Å; Bi–N 2.384(4) Å; Bi–Cl = 2.562(1) Å).

Another Bi(III) pyridinedicarboxylate complex $[pydaH]_2[Bi_2(pydc)_4(H_2O)_2]\cdot 4H_2O$, was prepared from bismuth(III) subnitrate $Bi_5O(OH)_9(NO_3)_4$ and $(pydaH_2)^{2+}(pydc)^{2-}$, where pyda is pyridine-2,6-diamine [50]. In the structure of the centrosymmetric anion $[Bi_2(pydc)_4(H_2O)_2]^{2-}$ each bismuth(III) is coordinated by two pyridine-2,6-dicarboxylate ions, a bridging carboxylate oxygen atom and a water molecule (Bi–O 2.327(3)–2.589(3) Å; Bi–N 2.435(3) and 2.555(3) Å).

The structural data concerning bismuth(III) complexes with monoaminopolycarboxylate ligands are presented in Table 2.

3. Bismuth(III) complexes with diaminopolycarboxylate ligands

Bismuth complexes with anions of ethylenediaminetetraacetic acid (H_4edta) are far the most widely investigated of the diaminopolycarboxylates because the acid and its disodium salt are readily available and form stable complexes with the bismuth(III) ion in aqueous solutions. As a result, there is a substantial literature dealing with the study of bismuth(III) ethylenediaminetetraacetates while the data concerning other diaminopolycarboxylatobismuthates(III) are more limited.

The structural data for bismuth(III) complexes with anions of diaminopolycarboxylic acids are collected in Tables 3 and 4 (mixed-ligand complexes).

3.1. Bi(III) complexes with ethylenediaminetetraacetate ligands

Due to the large volume of data, Bi(III) complexes with edta will be further subdivided according to the charge, nature and composition of the outer-sphere cation and the presence of additional ligands in the coordination sphere of Bi(III) (mixed-ligand complexes).

3.1.1. Protonated Bi(III) ethylenediaminetetraacetate complexes

Bismuth(III) forms stable complexes with $edta^{4-}$ and this was demonstrated by means of several methods: spectrophotometry, potentiometry, polarography, as well as by IR and NMR spectroscopy. Bhat and Krishna Iyer [51] investigated the reaction of Bi(III) with H_4edta spectrophotometrically and by means of pH-metric titrations, the stability constant of the $[Bi(edta)]^-$ complex was 26.47.

The complexation reaction of Bi(III) and $edta^{4-}$ has been also studied spectrophotometrically [52]. In the pH range 0.6–1.4, the formation of the 1:1 protonated complex [Bi(Hedta)] has been proposed, while at pH 1.5–10 the $[Bi(edta)]^-$ exists. At higher pH the hydrolysis occurs with the formation of bismuth hydroxide. The stability constants of the protonated and anionic complex were 17.73 and 25.68, respectively. The polarimetric studies showed, however, slightly higher values, 26.41 [26], 27.93 [53], and 27.94 [54].

Table 4
Structural features of bismuth(III) mixed-ligand diaminopolycarboxylates

Compound	CN, polyhedron	Type of structure	Bond distances (Å)			References
			d(Bi–N)	d(Bi–O)	d(Bi–E)	
$[Bi(Hedta)(tu)_2]$	8, SA	Monomeric	2.510(7) × 2	2.378(7) × 2, 2.521(9) × 2	3.035(4) × 2	[92]
$Li[Bi(edta)(tu)_2]\cdot 5.5H_2O$	Bi(1) 8, SA		2.498(2), 2.498(2)	2.393(1), 2.484(1), 2.484(1), 2.563(1)	2.9877(6), 3.0429(7)	[93]
	Bi(2) 8, SA	Monomeric	2.499(2), 2.505(2)	2.358(1), 2.424(1), 2.436(1), 2.493(1)	3.0726(6), 3.2088(6)	
$K[Bi(edta)(tu)_2]$	8, SA	Monomeric	2.466(2), 2.481(1)	2.362(2), 2.410(2), 2.410(2), 2.483(1)	3.0909(7), 3.226(8)	[94]
$Rb[Bi(edta)(tu)_2]$	8, SA	Monomeric	2.471(2), 2.482(2)	2.351(1), 2.402(1), 2.406(1), 2.475(1)	3.1366(6), 3.2425(7)	[95]
$Cs[Bi(edta)(tu)_2]\cdot 3H_2O$	Bi(1) 8, SA	Monomeric	2.506(2) × 2	2.413(2) × 2, 2.434(2) × 2	3.1177(7) × 2	[95]
	Bi(2)		2.498(2) × 2	2.416(2) × x2, 2.480(2) × 2	3.0398(8) × 2	
$(CH_7N_4)[Bi(edta)(tu)_2]\cdot 2.5H_2O$	8, SA	Monomeric	2.476(1), 2.529(1)	2.379(1), 2.399(1), 2.408(1), 2.546(1)	3.0110(5), 3.1044(5)	[96]
$(CH_7N_4)[Bi(edta)(tu)(H_2O)]\cdot 2H_2O$	8, SA	Monomeric	2.480(1), 2.497(2)	2.377(1), 2.434(1), 2.438(1), 2.446(1)	2.604(1) (H_2O) 3.1665(7) (S)	[96]
$(CH_7N_4)[Bi(edta)Cl]$	8, SA	Polymeric (chain)	2.465(2), 2.530(2)	2.330(1), 2.356(1), 2.464(1), 2.524(1), 2.707(1)[a]	2.9212(6) (Cl)	[97]
$[Co(NH_3)_5(NCS)]_2[(edta)Bi(\mu\text{-}C_2O_4)Bi(edta)]\cdot 12H_2O$	8, BTP	Dimeric	2.520(6), 2.540(7)	2.328(6), 2.454(6), 2.481(5), 2.598(6)	2.523(6) (C_2O_4) 2.540(7) (C_2O_4)	[98]
$[Co(Hchdd)_2(an)_2][Bi(edta)(H_2O)]\cdot 3.5H_2O$	Bi(1) 7 + 1, BTP	Monomeric	2.47(1), 2.478(9)	2.270(8), 2.43(1), 2.420(8), 2.50(2)	2.59(1) (H_2O) 3.143(8) (oxime)	[87]
	Bi(2)		2.50(1), 2.485(8)	2.232(9), 2.42(1), 2.442(9), 2.45(1)	2.57(1) (H_2O) 3.013(8) (oxime)	
$[NdBi(edta)(NO_3)_2(H_2O)_{7.22}]_n$	Bi(1) 9 + 1, no data	Bimetallic polymer	2.487(3), 2.493(4);	2.357(3), 2.434(3), 2.482(3), 2.504(3),	2.493(4) (NO_3) 3.005(3) (NO_3)	[99]
	Bi(2) 7 + 1, no data		2.429(3), 2.477(4)	2.357(3), 2.434(3), 2.482(3), 2.504(3)	2.493(4) (NO_3) 3.005(3) (NO_3)	

[a] Bridging Bi–O(carbonylic), E–O, S or Cl donors of additional ligand/ligands.

In solid state Bi(III) forms with edta two types of complexes: protonated neutral [Bi(Hedta)] and deprotonated anionic $[Bi(edta)]^-$ species. Synthesis of an acidic complex formulated as Bi(Hedta) was reported by Brintzinger and Munkelt as early as in 1948 [55]. Bhat and Krishna Iyer reported the synthesis of the same acidic complex, but based on the results of the elemental analysis it was formulated as $Bi(Hedta)\cdot H_2O$ [51]. The same authors investigated the thermal stability of this complex in an atmosphere of air and nitrogen [56]. The IR spectrum of $Bi(Hedta)\cdot H_2O$ showed that all four acetate groups are coordinated to Bi, and $Hedta^{3-}$ may be functioning as a hexadentate ligand [57].

Ambiguous data about Bi(III)–edta complexes prompted one of the authors in the late 80s to initiate a systematic study [58–61]. $Bi(OH)_3$, Bi_2O_3, BiF_3 or $(BiO)_2CO_3$ dissolve readily in the presence of H_4edta in aqueous solutions, giving rise to protonated $Bi(Hedta)\cdot nH_2O$ chelates. Depending on the conditions of crystallization, the latter can be obtained as anhydrous Bi(Hedta) or as a dihydrate, $Bi(Hedta)\cdot 2H_2O$. Both IR and powder X-ray diffraction data showed that the dihydrate forms two polymorph modifications, rhombic (α) and prismatic (β). Anhydrous Bi(Hedta) can be obtained by fast crystallization of the complex from hot aqueous solutions or by dehydration of the dihydrate. The corresponding dihydrate is obtained by crystallization from dilute solutions at room temperature.

The IR spectra of α-$Bi(Hedta)\cdot 2H_2O$ and β-$Bi(Hedta)\cdot 2H_2O$ are practically identical [58]. In solid state [Bi(Hedta)] shows a polymeric structure, with the ligand $(Hedta)^{3-}$ having a hexadentate–chelate (4O + 2N) and di-bridging (2O) function [59]. Bi(III) has an eight-coordinate distorted antiprismatic environment imposed by four Bi–O chelate bonds (Bi–$O_{chelate}$ 2.399(3) × 2 Å and 2.472(4) × 2 Å), two Bi–O bridging bonds (Bi–$O_{bridging}$ 2.617(5) × 2 Å), and two relatively strong Bi–N bonds (Bi–N 2.465(5) × 2 Å). A peculiarity of this complex is the presence of a strong intermolecular hydrogen bond. The proton of the $(Hedta)^{3-}$ is situated between two acetate groups of the neighboring complexes. The same inversion-symmetric position of H^+ was observed in the structure of $(NH_4)[Bi_2(Hedta)(edta)]\cdot 2H_2O$ [62].

The Bi–O bridging bonds in β-$[Bi(Hedta)]\cdot 2H_2O$ [60] are close to those in [Bi(Hedta)] (2.697(8) and 2.679(9) versus 2.617(5) × 2 Å). However, two of the four chelate Bi–O bonds are slightly shorter (Bi–O(3) 2.231(8) and Bi–O(6) 2.249(9) Å) than the corresponding bonds in Bi(Hedta). The hydrogen atom (H(4)) on Hedta ligand occupies the center of inversion and is common for two carboxylate groups. The H(4) atom is also involved in formation of a strong hydrogen bond (O(4)···H(4)···O(w) 2.50(1) Å), but in this case the acceptor is the oxygen atom of a water molecule.

The structure of the rhombic modification, α-$[Bi(Hedta)]\cdot 2H_2O$ [61], is formed by neutral complexes [Bi(Hedta)] and lattice water molecules. The coordination environment for Bi is identical to that observed in the case of β-$[Bi(Hedta)]\cdot 2H_2O$. By means of bridging oxygen atoms [Bi(Hedta)] complexes are connected in polymeric layers (Fig. 6).

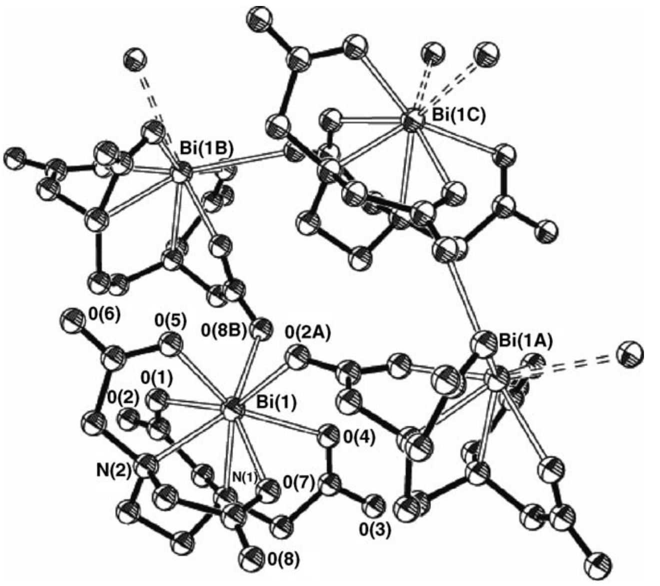


Fig. 6. ADE drawing of a fragment of the polymeric layer in α-$[Bi(Hedta)]\cdot 2H_2O$.

3.1.2. Bi(III) ethylenediaminetetraacetate complexes with alkali metal and ammonium cations

The carboxylate proton in [Bi(Hedta)] has a significant acidity, the aqueous solutions showing a pH ∼ 2. Reactions of aqueous solutions of [Bi(Hedta)] and alkali metal or ammonium carbonates M_2CO_3 have been investigated for different molar ratios and at different pH (from 2.5 to 9). In the range of pH $6-9$, the corresponding salts, $MBi(edta)\cdot nH_2O$ (where $n = 4$ for $M^+ = Li^+$; $n = 3$ for $M^+ = Na^+$, K^+ and Rb^+ and $n = 1$ for Cs^+ and NH_4^+), can be isolated [63].

Thermogravimetric studies in air showed that the dehydration of $KBi(edta)\cdot 3H_2O$ and $RbBi(edta)\cdot 3H_2O$ starts at 50 °C. Water is completely removed from the compounds at 210 °C. Thermal pyrolysis starts at 260 °C. In contrast, $CsBi(edta)\cdot H_2O$ is stable up to 100 °C, and the dehydration occurs between 140 and 260 °C. The complex decomposes above 260 °C. A similar thermal behavior in air was established for some of the ethylenediaminetetraacetatobismuthates(III) of divalent metals [64–66]. Heating $NaBi(edta)\cdot 3H_2O$ in an atmosphere of sulphur vapors between 600 and 900 °C leads to the mixed sulphide $NaBiS_2$ [67].

Reacting aqueous [Bi(Hedta)] with M_2CO_3 in molar ratios from 0.25:1.0 to 0.5:1.0 at pH 3–4, complexes of the general formula $MBi_2(Hedta)(edta)\cdot nH_2O$ ($n = 2$ for $M^+ = K^+$, Rb^+, NH_4^+ and $n = 3$ for $M^+ = Cs^+$) were synthesized [63]. The same complexes can be obtained by mixing aqueous MCl and $[Bi(Hedta)]\cdot 2H_2O$ in molar ratios from 1:1 to 5:1 at pH ≈ 3 or by addition of a diluted solution of hydrochloric acid to a solution of $MBi(edta)\cdot nH_2O$ until pH ≈ 3 is reached. The complexes crystallize from concentrated solution and are slightly soluble in water. Addition of corresponding K^+, Rb^+, Cs^+ or NH_4^+ carbonates or hydroxides to the aqueous $MBi_2(Hedta)(edta)\cdot nH_2O$ and adjustment of pH to 6–8 leads to $MBi(edta)\cdot nH_2O$.

The following alkali metal and ammonium ethylenediaminetetraacetatobismuthates(III) have been structurally characterized: Li[Bi(edta)]·4H_2O [68], Na[Bi(edta)]·3H_2O [67,69], Rb[Bi(edta)]·3H_2O [70], Cs[Bi(edta)]·H_2O [71], and NH_4[Bi(edta)]·H_2O [59]. The crystal structure of Li[Bi(edta)]·4H_2O [68] contains hydrated $Li(H_2O)_2^+$ cations, complex $[Bi(edta)]^-$ anions, and water molecules of crystallization. The $Li(H_2O)_2^+$ cations link the $[Bi(edta)]^-$ anions in polymeric chains via two carbonyl oxygen atoms. The coordination environment of Bi(III) contains four oxygen and two nitrogen atoms of the $edta^{4-}$ ligand and two O atoms from two neighboring $[Bi(edta)]^-$ anions. The Bi–N distances are equal to 2.432(3) and 2.446(3) Å, Bi–O chelate distances vary from 2.281(3) to 2.462(3) Å, while the bridging interactions are 2.866(3) and 3.178(3) Å, typical for bridging Bi–O bonds in Bi(III) PAPC complexes.

In Na[Bi(edta)]·3H_2O [67,69] the bismuth coordination environment can be presented as square antiprismatic and includes two nitrogen atoms (Bi–N 2.491(9) and 2.497(8) Å), four oxygen atoms of carboxylate groups (Bi–O chelate 2.324(8), 2.331(8), 2.362(8), and 2.525(8) Å), and two oxygen atoms of neighboring complexes (Bi–O bridging 2.637(8) and 2.843(8) Å). The latter results in the formation of layers. The Na^+ cation has an octahedral coordination environment, formed by three O atoms of water molecules and three O atoms of edta. In the crystal structure of Na[Bi(edta)]·3H_2O the complex anions $[Bi(edta)]^-$ are joined in layers by means of oxygen atoms. The polymeric layers are connected by cyclic carboxylate dimers. The 3D structure is completed by dimers between two Na^+ cations (Na···Na distance is 3.92(1) Å) connected by two bridging water molecules [67].

Crystal structures of isostructural K[Bi(edta)]·3H_2O and Rb[Bi(edta)]·3H_2O [70] contain octa-coordinate Bi(III) with bonding to six $edta^{4-}$ donor atoms and two bridging carboxylate oxygen atoms of the neighboring complexes. By means of this bridging $[Bi(edta)]^-$ anions the complexes are joined into polymeric layers (Fig. 7). The coordination environment of Rb^+ includes eight O atoms: three O atoms of water molecules, the Bi–O–Rb bridging O atom, and four oxygen atoms of an $edta^{4-}$ ligand.

The crystal structure of Cs[Bi(edta)]·H_2O [71] contains two types of Cs^+ cations with an occupancy factor of 0.5, polymeric $[Bi(edta)]_n^{n-}$ anions, and lattice water molecules. The Bi–O bond lengths with the chelate oxygen atoms of edta vary from 2.302(2) to 2.599(2) Å, and the Bi–N bond lengths are 2.493(2) and 2.513(2) Å. The distances from bismuth to the bridging O atoms are 2.722(3) and 2.876(2) Å. By means of one bridging oxygen atom, the $[Bi(edta)]^-$ complexes are joined in centrosymmetric dimers, while the second bridging oxygen atom connects the dimers into zigzag polymeric chains.

The corresponding ammonium salt, NH_4[Bi(edta)]·H_2O [59] contains Bi atoms in a distorted antiprismatic environment that involves, as in M[Bi(edta)]·3H_2O ($M^+ = Na^+$, K^+, Rb^+) [67,69,70] and Cs[Bi(edta)]·H_2O [71], six O donor atoms of the $edta^{4-}$ ligand and two bridging oxygen atoms of neighboring complexes. The lengths of the chelate Bi–O bonds vary from 2.290(9) to 2.494(8) Å, and the Bi–N bond lengths are 2.479(9) and 2.490(10) Å, while the distances from the Bi atom to the two bridging O atoms are 2.792(9) and 2.805(8) Å.

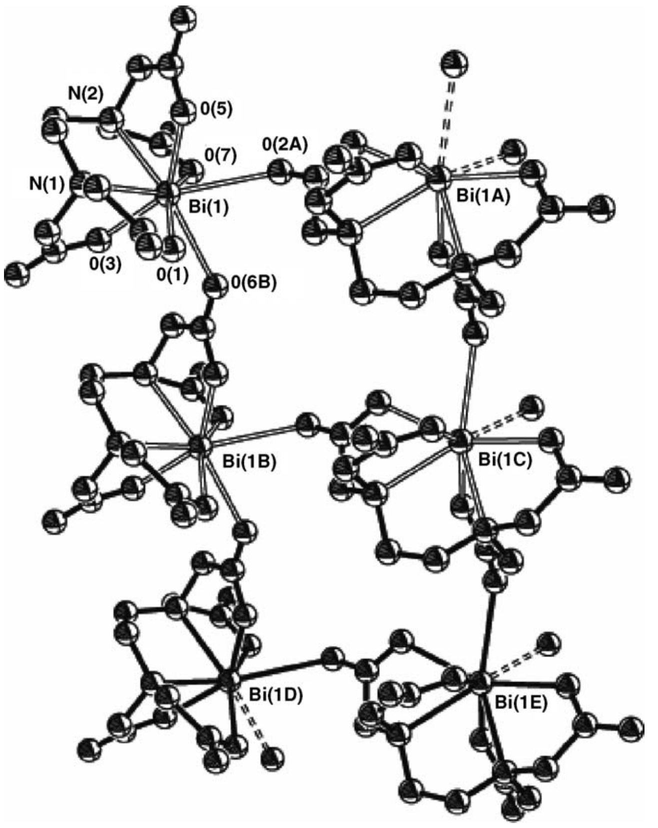


Fig. 7. ADE drawing of a fragment of the $[Bi(edta)]^-$ polymeric layer in Rb[Bi(edta)]·3H_2O.

In a series of complexes such as M[Bi(edta)]·nH_2O, it is interesting to compare the influence of the cation on the structures of the complexes. Thus, in the crystal structure of Li[Bi(edta)]·4H_2O there is no contact between Li and Bi atoms, while M[Bi(edta)]·3H_2O ($M^+ = Na^+$, K^+, Rb^+) [67,69,70] and Cs[Bi(edta)]·H_2O [71] structures contain oxygen bridges between the monovalent cation and the Bi(III) centers. In Na[Bi(edta)]·3H_2O the distance Na···Bi 4.02(1) Å is practically identical to the sum of van der Waals radii of these atoms (3.99 Å [72]), while in CsBi(edta)·H_2O and RbBi(edta)·3H_2O, the Cs···Bi and Rb···Bi distances are about 0.2 Å and, respectively, 0.3 Å less than this value [72]. There is also an influence of the size and nature of the counter cation on the structure of the Bi complexes. For instance, the cations with small radii, Li^+ (CN = 4) and Na^+ (CN = 6), form layer polymeric structures. Larger cations, K^+ and Rb^+ (CN = 8–10), also form layer polymeric structures with short contacts between cations and Bi(III), while the largest in this series, Cs^+ (CN = 12), forms chain structures.

The X-ray powder diffraction analysis showed that the M[Bi_2(Hedta)(edta)]·2H_2O complexes, where $M^+ = K^+$, Rb^+, NH_4^+ are isostructural, while the Cs^+ salt Cs[Bi_2(Hedta)(edta)]·3H_2O is not a part of this series [62,73]. It has been shown that in the crystal structure of Cs[Bi_2(Hedta)(edta)]·3H_2O [73], the “odd” hydrogen atom of $Hedta^{3-}$ is randomly disordered over the two ligands. The Bi atom is coordinated by six donor atoms of the edta (Bi–O 2.282-2.599 Å, Bi–N 2.451 and 2.503 Å), and two bridging oxygen atoms (Bi–$O_{bridging}$ 2.971 and 2.774 Å). In the structure of $Cs[Bi_2(Hedta)(edta)]\cdot 3H_2O$ as in structures of other protonated Bi(III)–edta complexes [59–61], and in $[Sb(Hedta)]\cdot 2H_2O$ [74], Bi(Sb)–O bonds with the carbonyl oxygen atoms of COOH groups are normally longer than other Bi(Sb)–O bonds in the polyhedron. By means of one Bi–O bridging bond the $[Bi(edta)]^-$ complexes form centrosymmetric dimers, while by means of double bridges the Bi polyhedra form bent twin polymeric chains.

The independent part of the $NH_4[Bi_2(Hedta)(edta)]\cdot 2H_2O$ structure [62], a member of the isostructural series $M[Bi_2(Hedta)(edta)]\cdot 2H_2O$ (M = K, Rb, NH_4), contains an eight-coordinated Bi atom, "semiprotonated" $Hedta^{3-}$ ligand and one water molecule randomly disordered over two positions with an occupancy factor of 0.6 and 0.4, respectively. The coordination environment of Bi is formed by two nitrogen donor atoms, three oxygen atoms of deprotonated carboxylate groups, one carbonyl oxygen atom of a "semiprotonated" ligand, and two bridging oxygen atoms of the neighboring complexes. Like in the case of the corresponding cesium complex, the $[Bi_2(Hedta)(edta)]^-$ moieties form bent twin polymeric chains.

3.1.3. Bi(III) ethylenediaminetetraacetate complexes with divalent metal cations

Ethylenediaminetetraacetatobismuthates(III) with divalent metal cations of the general formula $M\{Bi(edta)\}_2\cdot nH_2O$ (where M(II) = Mg(II), Ca(II), Sr(II), Ba(II), Ni(II), Co(II), Cu(II), Zn(II), Cd(II), n = 2–9) were also described. The preparative methods include reaction of [Bi(Hedta)] with the appropriate carbonates or basic metal carbonates in aqueous solutions [64,65] or via exchange reactions of $Ba\{Bi(edta)\}_2$ with corresponding divalent metal sulphates [66]. Polymeric motifs have been found in crystal structures of all characterized complexes of this type: $Ca[Bi(edta)]_2\cdot 9H_2O$ [75], $Ba[Bi_2(edta)_2(H_2O)]\cdot H_2O$ [76] and in isostructural complexes $Co[Bi(edta)]_2\cdot 9H_2O$, $Ni[Bi(edta)]_2\cdot 9H_2O$ [77], and $Cu[Bi(edta)]_2\cdot 9H_2O$ [65].

In the crystal structure of $Ca[Bi(edta)]_2\cdot 9H_2O$ [75] the $edta^{4-}$ ligand coordinates one Bi(III) center by means of two nitrogen and four oxygen atoms (Bi–N 2.460(6) and 2.543(6) Å, Bi–O 2.360(6)–2.463(7) Å). Two bridging carboxylate oxygen atoms of two neighboring complexes complete the slightly distorted square antiprismatic environment of Bi. The distance from the Bi atom to the carbonyl bridging atom is 2.778(6) Å, while the distance to the chelate carboxylic oxygen atom of neighboring complex is 3.038 Å, one of the longest in Bi(III) ethylenediaminetetraacetate complexes.

The corresponding cobalt [77], nickel [77] and copper [65] complexes, $M[Bi(edta)]_2\cdot 9H_2O$, are isostructural. The $edta^{4-}$ ligand exhibits a hexadentate–chelate (4O + 2N) and di-bridging function (2O). By means of two chelate oxygen atoms the square antiprismatic polyhedra of bismuth(III) form centrosymmetric dimers. The dimers are further connected by means of double bridges in polymeric chains. The average value of Bi–N bonds in the three complexes is 2.44(5) Å and is about 0.1 Å shorter that the corresponding bond in $Ca[Bi(edta)]_2\cdot 9H_2O$. In contrast, the Bi–O bonds in the three isostructural complexes $M[Bi(edta)]_2\cdot 9H_2O$ are slightly longer (0.01–0.03 Å).

Thermal decomposition of $Cu[Bi(edta)]_2\cdot 9H_2O$ has been investigated by TG and HTXRD. It was established that the complex produces $Cu[Bi(edta)]_2\cdot 4H_2O$ between 40 and 60 °C; above 120 °C $Cu[Bi(edta)]_2$ is formed and is stable up to 200 °C. The pyrolysis results in the pure perovskite-phase Bi_2CuO_4 at a relatively low temperature, 360 °C. Thus, $Cu[Bi(edta)]_2\cdot 9H_2O$ can be considered as a suitable single-molecular precursor for bismuth cuprate.

The $Ba[Bi_2(edta)_2(H_2O)]\cdot H_2O$ [76] crystals are triclinic, in which two crystallographically independent $[Bi(edta)]^-$ complexes and the coordination water molecule form tetranuclear associates. The environments of two independent bismuth atoms (CN = 8) are similar, and their polyhedra can be described as distorted dodecahedra. A coordinated water molecule serves as a bridge between the two Bi centers [76]. The two crystallographically independent Bi atoms have an octa-fold coordination environment that includes six donor atoms from the $edta^{4-}$ ligand (Bi–O 2.27–2.52, respectively 2.26–2.47 Å; Bi–N 2.47, 2.48 and 2.44 and 2.49 Å), O atom of a water molecule (Bi–O_w 2.73 and 2.66 Å), and a bridging carbonyl O(4)′ atom of the neighboring complex (Bi–O(4)′ 2.78, and 2.97 Å).

3.1.4. Bi(III) ethylenediaminetetraacetate complexes with protonated organic base cations

Synthesis and characterization of several Bi(III)–edta complexes with some protonated organic base cations (guanidinium [78,79], aminoguanidinium [79], ethylenediammonium [80], β-alaninium [81], and thiosemicarbazidium [82]) have been reported.

The guanidinium salt $(CH_6N_3)Bi(edta)\cdot H_2O$ was obtained by reaction of BiF_3 and H_4edta, with subsequent addition of guanidinium carbonate to achieve a neutral or slightly basic pH. The same compound can be isolated by reaction of aqueous solutions of [Bi(Hedta)] with guanidinium carbonate or guanidinium chloride. The corresponding Bi–edta complex with aminoguanidinium $(CH_7N_4)Bi(edta)$, can be obtained similarly, but it contains no water molecules [79].

$(CH_6N_3)[Bi(edta)(H_2O)]$ was the first structurally characterized Bi–edta complex [78]. Rhombic crystals of $(CH_6N_3)[Bi(edta)(H_2O)]$ are built by $(CH_6N_3)^+$ cations and $[Bi(edta)(H_2O)]^-$ anions. The coordination polyhedron around the metal may be described as a distorted square antiprism with a hexadentate edta ligand (Bi–N 2.494(4) and 2.522(4) Å, Bi–O 2.352(4)–2.452(4) Å), a coordinated water molecule (Bi–O_w 2.68(1) Å), and a bridging oxygen carbonyl atom of the neighboring complex (Bi–O 2.70(1) Å), that generates spiral polymeric chains.

Addition of ethylenediamine (en) to aqueous [Bi(Hedta)] up to pH 7 leads to isolation of $(enH_2)[Bi(edta)(H_2O)]_2\cdot 4H_2O$ [80]. The anionic sub-lattice is formed by polymeric complexes $[Bi(edta)(H_2O)]_n^{n-}$ (Fig. 8). The distorted square antiprismatic environment of Bi is formed by hexadentate $edta^{4-}$ (Bi–N 2.48(1) and 2.49(1) Å, Bi–O 2.291(9)–2.476(9) Å), a coordinated water molecule (Bi–O_w 2.87(1) Å), and the bridg-

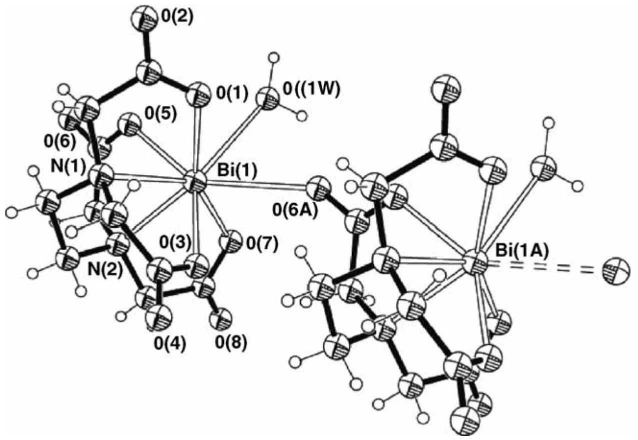


Fig. 8. ADE representation of a fragment of the polymeric chain in $(enH_2)[Bi(edta)(H_2O)]_2·4H_2O$.

ing carbonyl O(6A) atom (Bi–O(6A) 2.82(1) Å) of the next complex.

Reaction of β-alanine and $[Bi(Hedta)]·2H_2O$ in aqueous solutions has been investigated in the range of molar ratios from 1:1 to 5:1, but only one compound crystallizes: $(H_3NCH_2CH_2CO_2H)[Bi(edta)(H_2O)]$. At higher molar ratios (5:1) β-alanine also crystallizes. $(H_3NCH_2CH_2CO_2H)[Bi(edta)(H_2O)]$ loses water upon heating to 130 °C. The complex $(H_3NCH_2CH_2CO_2H)[Bi(edta)(H_2O)]$ is the first example of Bi(III)–edta complexes with a protonated aminoacid [81]. The crystal structure of $(H_3NCH_2CH_2CO_2H)[Bi(edta)(H_2O)]$ is formed by protonated $(H_3NCH_2CH_2CO_2H)^+$ cations and dimeric $[Bi(edta)(H_2O)]_2{}^{2-}$ anions (Fig. 9), joined together by electrostatic forces and hydrogen bonds in a 3D network. The dimeric anion contains Bi(III) in a distorted trigonal dodecahedral environment, including two nitrogen (Bi–N 2.426(7) and 2.492(7) Å) and four oxygen donor atoms of a chelate edta, a coordinated water molecule (Bi–O_W 2.727(8) Å), and a bridging cyclic O(1A) atom of the dimer partner (Bi–O(1A) 2.768(8) Å).

The thiosemicarbazidium ethylenediaminetetraacetatobismuthate(III) $(CH_6N_3S)Bi(edta)·H_2O$, was isolated from aqueous solutions containing thiosemicarbazide and $[Bi(Hedta)]·2H_2O$ in molar ratios from 1:1 to 5:1. However, for 4:1 and 5:1 molar ratio reactions, the complex contains traces of thiosemicarbazide. $(CH_6N_3S)[Bi(edta)(H_2O)]$ is a remarkable Bi–edta complex, showing for the first time a CN 7 of Bi(III) [82].

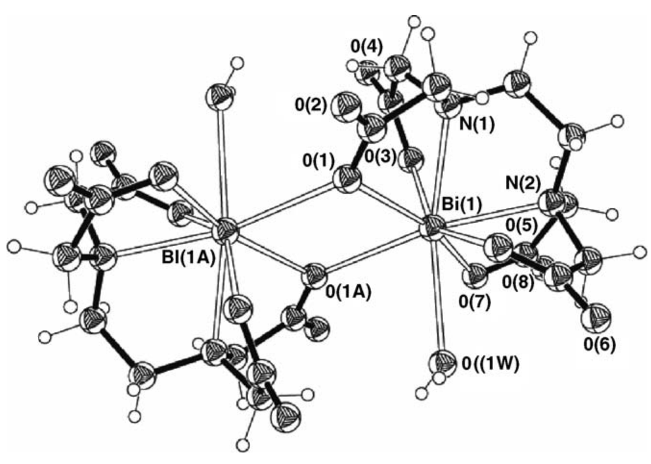


Fig. 9. ADE representation the structure of the dimeric anion $[Bi(edta)(H_2O)]_2{}^{2-}$ in $(H_3NCH_2CH_2CO_2H)_2[Bi(edta)(H_2O)]_2$.

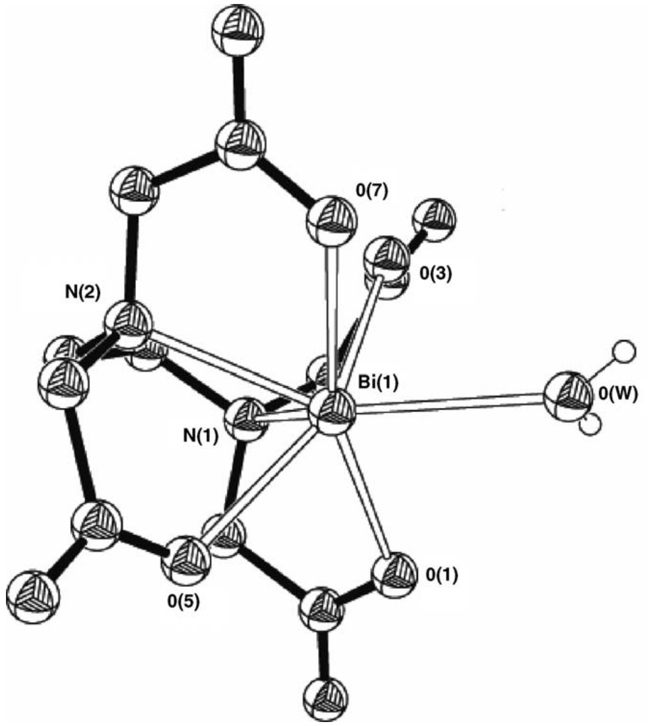


Fig. 10. ADE drawing of the complex anion in $(CH_6N_3S)[Bi(edta)(H_2O)]$.

The structure of the complex anion $[Bi(edta)(H_2O)]^-$ in $(CH_6N_3S)[Bi(edta)(H_2O)]$ is presented in Fig. 10. The coordination environment of the bismuth atom includes six donor atoms of $edta^{4-}$ ligand (Bi–N 2.453(2) and 2.487(2) Å, Bi–O 2.348(2), 2.362(2), 2.391(2), 2.486(2) Å) and a coordinated water molecule.

The crystal structure of the aminoguanidinium complex $(CH_7N_4)[Bi(edta)]$, contains no water molecules and is formed from monovalent $(CH_7N_4)^+$ cations and polymeric $[Bi(edta)]_n{}^{n-}$ anions [79]. The complex anion $[Bi(edta)]_n{}^{n-}$ has the Bi atom in a dodecahedral geometry. The coordination sites are occupied by six donor atoms of $edta^{4-}$, with Bi–N bonds of 2.454(4) and 2.492(4) Å, and three Bi–O bonds of 2.430 Å. The remaining two sites are occupied by a chelate bridging oxygen atom (Bi–O 2.657 Å) of one neighboring complex and a carbonyl oxygen atom (Bi–O 2.931 Å) of the second.

3.1.5. Bi(III) ethylenediaminetetraacetates with metal complex cations

In recent years, a number of Bi(III)–edta complexes, containing as counter-ion transition metal complex cations have been obtained and characterized. The Co(III)–Bi(III) complexes $[Co(NH_3)_4(CO_3)][Bi(edta)]·3H_2O$ [83] and $[Co(NH_3)_4(C_2O_4)][Bi(edta)]·3H_2O$ [84,85] were isolated from aqueous solutions of $Na[Bi(edta)]·3H_2O$ in the presence of $[Co(NH_3)_4(CO_3)]^+$ and $[Co(NH_3)_4(C_2O_4)]^+$ salts. Both complexes have a polymeric structure. The bismuth polyhedra in the two complexes were described as square antiprismatic. The Bi–O and Bi–N bond lengths are quite similar for the two complexes (Table 3).

Trans-$[Co(NH_3)_4(NO_2)_2][Bi(edta)(H_2O)]\cdot 2H_2O$ was prepared by reaction of aqueous *trans*-$[Co(NH_3)_4(NO_2)_2]_2(SO_4)$ and $Ba[Bi(edta)]_2$. The same method was used to obtain $[Co(NH_3)_5(NCS)][Bi(edta)]_2\cdot 4H_2O$ [83]. *Trans*-$[Co(NH_3)_4(NO_2)_2][Bi(edta)(H_2O)]\cdot 2H_2O$ contains eight-coordinated Bi, bonded to an $edta^{4-}$ ligand (2N + 4O), and further, to complete the eight-coordination, a water molecule and an carbonyl oxygen of a carboxylate group of the neighboring unit to form dimers.

By means of TGA and HTXRD it has been established that the product of thermal decomposition in air of *trans*-$[Co(NH_3)_4(NO_2)_2][Bi(edta)(H_2O)]\cdot 2H_2O$, as well as for $[Co(NH_3)_4(CO_3)][Bi(edta)]\cdot 3H_2O$ is a sillenite-type phase $Bi_{26-x}Co_xO_{40-\delta}$, contaminated with small traces of Co_3O_4. The product of pyrolysis of $[Co(NH_3)_5(NCS)][Bi(edta)]_2\cdot 4H_2O$ is an unidentified polyphasic crystalline material [83].

Antsyshkina and co-workers [84] obtained $[Co(NH_3)_2(ala)_2][Bi(edta)(H_2O)]\cdot 5H_2O$ by reaction of $[Co(NH_3)_2(ala)_2]Cl$ or $[Co(NH_3)_2(ala)_2]ClO_4$ and $Na[Bi(edta)]\cdot 3H_2O$ in aqueous solutions. A particular feature of this complex is that practically all bond distances between Bi(III) and carboxylate oxygen atoms are equal (Bi–O 2.41–2.47 Å). The bond distances to the bridging oxygen atom and water molecule are longer, 2.68 and 2.73 Å, respectively. The structure is formed by cationic Co(III) complexes and polymeric $[Bi(edta)(H_2O)]^-$ anions.

Compounds of the general formula 1,6-$[Co(Hdiox)_2(L)_2][Bi(edta)]\cdot nH_2O$ (where Hdiox-monodeprotonated 2,3-butanedione-dioxime, Hdmg, and monodeprotonated 1,2-cyclohexanedione-dioxime, Hchdd, L, aniline or *o*-, *m*-, *p*-toluidine) were obtained by the exchange reaction of aqueous 1,6-$[Co(Hdiox)_2(L)_2]_2SO_4$ and $Ba[Bi(edta)]_2$ after removal of precipitated barium sulphate [86,87]. NMR spectroscopy in DMSO confirms the *trans*-configuration of the complex cations by observation of a broad singlet of two symmetric hydrogen bonds. The NCH_2CH_2N component of the $edta^{4-}$ ligand is in the fast exchange domain and the signal from this group is a singlet, while four acetate CH_2 protons give rise to an AB quartet system. It was shown that thermolysis of these complexes occurs in three successive stages: (i) dehydration, (ii) pyrolysis of the ligands and, (iii) the formation of a sillenite-type phase $Bi_{26-x}Co_xO_{40-\delta}$ and small quantities of Co_3O_4 [86–88].

Structures of three Co(III) dioximate-Bi(edta) complexes were reported: $[Co(Hdmg)_2(o\text{-tol})_2][Bi(edta)(H_2O)]\cdot 5H_2O$ [86], $[Co(Hchdd)_2(an)_2][Bi(edta)(H_2O)]\cdot 3.5H_2O$ [87], and $[Co(Hchdd)_2(p\text{-tol})_2][Bi(edta)]\cdot 4H_2O$ [87].

$[Co(Hdmg)_2(o\text{-tol})_2][Bi(edta)(H_2O)]\cdot 5H_2O$ contains $[Bi(edta)(H_2O)]_2^{2-}$ dimeric centrosymmetric anions with strongly distorted antiprismatic geometries about Bi centers. The structure of the doubly charged centrosymmetric anion is similar to the corresponding dimeric anion in $(H_3NCH_2CH_2CO_2H)[Bi(edta)(H_2O)]$ [81]. The $edta^{4-}$ ligand is coordinated by the bismuth atom in a hexadentate fashion (4O + 2N). The Bi–N and Bi–O interatomic distances are 2.453(5)–2.500(5) Å and 2.328(5)–2.497(4) Å, respectively. The bridging carboxylic oxygen atom binds bidentate two Bi(III) centers (Bi–O 2.497(4) and 2.812(4) Å, respectively).

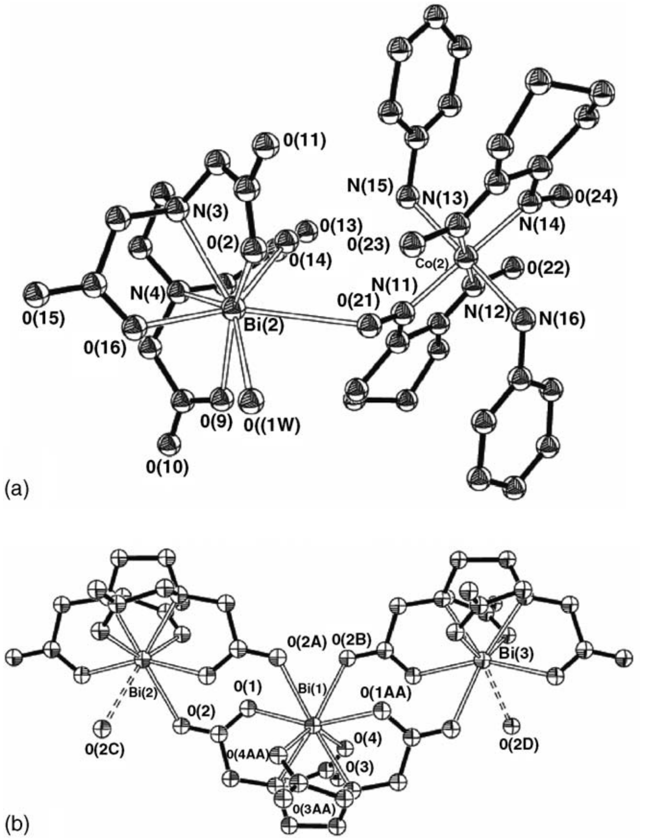


Fig. 11. ADE drawings of one independent unit of $[Co(Hchdd)_2(an)_2][Bi(edta)(H_2O)]\cdot 3.5H_2O$ (a), and a fragment of the polymeric anion in $[Co(Hchdd)_2(p\text{-tol})_2][Bi(edta)]\cdot 4H_2O$ (b).

In the crystal structures of $[Co(Hchdd)_2(an)_2][Bi(edta)(H_2O)]\cdot 3.5H_2O$ and $[Co(Hchdd)_2(p\text{-tol})_2][Bi(edta)]\cdot 4H_2O$ substitution of the aniline by *p*-toluidine in axial positions of the complex cations leads to radical changes in the anionic sub-lattice: from monomeric in the former complex to polymeric in the latter. Fig. 11(a) presents the structure of the complex cation and anion in one independent unit of $[Co(Hchdd)_2(an)_2][Bi(edta)(H_2O)]\cdot 3.5H_2O$ and the contact between them through a bridging O atom of the oxime group. The polymeric complex anion in $[Co(Hchdd)_2(p\text{-tol})_2][Bi(edta)]\cdot 4H_2O$ is shown in Fig. 11(b). For the aniline derivative, $edta^{4-}$ carries out a hexadentate–chelate (4O + 2N) function, while for the *p*-toluidine derivative the coordination capacity of the $edta^{4-}$ is increased up to 8, exhibiting a hexadentate–chelate (4O + 2N) and double-bridging (2O) function. The switch from aniline to *p*-toluidine in the Co(III) cation is accompanied by a dramatic change in the structure of the Bi–edta moiety, from monomeric to polymeric; moreover, the water molecule is expelled from the Bi(III) coordination sphere. These rather unexpected experimental results may be explained by a steric effect of the methyl groups that could be an impediment in efficient approaching of the complex cation and anion to form bridging oxime bonds. Hydrogen bond interactions and crystal packing forces may be affected, too.

This is supported by the comparing the structures of the two above-mentioned complexes with formally their closest analogue [Co(Hdmg)$_2$(*o*-tol)$_2$][Bi(edta)(H$_2$O)]·5H$_2$O [86]. In the latter the water molecule is still present, but no bridging oxime contact was noticed.

A heterobimetallic cation–anion Cu(II)–Bi(III) ethylenediaminetetraacetate complex [Cu(Hssa)(H$_2$O)][Bi(edta)(H$_2$O)]·3.88H$_2$O (Hssa = monodeprotonated anion of salicylaldehyde semicarbazone) was synthesized and structurally investigated [89]. The structure is built by complex cations [Cu(Hssa)(H$_2$O)]$^+$, centrosymmetric dimeric complex anions [Bi(edta)(H$_2$O)]$_2{}^{2-}$, and lattice water molecules. By means of the coordination bonds between Cu atoms and carbonylic oxygen atoms of the edta^{4-} ligands of the dimeric anion (Cu–O(8) 2.016(1) Å), complex cations [Cu(Hssa)(H$_2$O)]$^+$, two by two, are bonded with dimeric complex anions [Bi(edta)(H$_2$O)]$_2{}^{2-}$, resulting in tetranuclear units, which are linked by hydrogen bonds in a 3D framework.

3.1.6. Mixed-ligand Bi(III) ethylenediaminetetraacetate complexes

The formation of mixed-ligand complexes [Bi(edta)X]$^-$ (X (monodentate ligand), Br$^-$, I$^-$, SCN$^-$, NO$_2{}^-$, S$_2$O$_3{}^{2-}$, SO$_3{}^{2-}$ OH$^-$ and tu) have been investigated by means of potentiometry, IR, and NMR analyses [90]. The stability constants of both [Bi(edta)]$^-$ and [Bi(edta)X]$^{2-}$ complexes have been determined. The value of the [Bi(edta)(OH)]$^{2-}$ complex was reported to be 31.1, in good agreement with the previously reported value of 31.2 [41].

The reaction of [BiCl$_6$]$^{3-}$ with H$_4$edta in aqueous solutions was studied by potentiometry and the formation in the range $1.72 < \text{pH} < 3.03$ of a mixed ligand complex [Bi(Hedta)Cl$_2$]$^{2-}$ ($\log \beta = 19.44$) was presumed [41]. According to the same authors, at $3.03 < \text{pH} < 7.25$ the complex [Bi(Hedta)Cl]$^-$ dominated ($\log \beta = 23.69$), while between pH 7.25 and 9 the hydroxocomplex is dominant ($\log \beta = 31.20$). At pH > 9, decomposition of the complex and sedimentation of Bi(OH)$_3$ was observed.

The formation of mixed-ligand Bi(edta)–thiourea (tu) complexes was first detected in aqueous solutions [90]. Later, a variety of Bi(III) mixed-ligand complexes containing edta^{4-} and thiourea were isolated [91] and structurally characterized, namely [Bi(Hedta)(tu)$_2$] [92], Li[Bi(edta)(tu)$_2$]·5.5H$_2$O [93], M[Bi(edta)(tu)$_2$] (M = NH$_4$, K, Rb) [94,95], Cs[Bi(edta)(tu)$_2$]·3H$_2$O [95], (CH$_7$N$_4$)[Bi(edta)(tu)$_2$]·2.5H$_2$O [96], and (CH$_7$N$_4$)[Bi(edta)(tu)(H$_2$O)]·2H$_2$O [96].

[Bi(Hedta)(tu)$_2$] [91,92] has been prepared by reaction of aqueous [Bi(Hedta)]·2H$_2$O and tu in the molar ratio 1:3 and crystallization by slow evaporation of the obtained solution. M[Bi(edta)(tu)$_2$] and M[Bi(edta)(tu)$_2$]·nH$_2$O complexes were obtained by reaction of aqueous M[Bi(edta)]·nH$_2$O and tu in a 1:2 ratio. The complexes were isolated by slow evaporation of the resulting solutions in the dark.

The reaction of [Bi(Hedta)]·2H$_2$O with aminoguanidinium hydrogenocarbonate (CH$_7$N$_4$)HCO$_3$ and thiourea in 1:1:1 ratio at pH 3 results in formation of (CH$_7$N$_4$)[Bi(edta)]. For a ratio of the starting reagents 1:2:2 or 1:2:3 two complexes can be isolated, namely (CH$_7$N$_4$)[Bi(edta)(tu)$_2$]·2.5H$_2$O and (CH$_7$N$_4$)[Bi(edta)(tu)(H$_2$O)]·2H$_2$O [96]. The former was isolated in the presence of an excess of tu, while the second crystallizes from a solution with a ratio tu:[Bi(Hedta)] less than 2.

The complexes M[Bi(edta)(tu)$_2$] (M$^+$ = K$^+$, Rb$^+$, NH$_4{}^+$) are isostructural. The band corresponding to the ν(C=S) bond in the IR spectra of the mixed-ligand edta-tu-containing complexes is not shifted in comparison with the corresponding ν(C=S) in IR spectrum of free thiourea, proving its weak coordination to the Bi(III) center. This was later confirmed by X-ray analysis.

The structure of [Bi(Hedta)(tu)$_2$] [92] exhibits Bi in a square antiprismatic geometry, with the coordination sites occupied by a hexadentate edta^{4-} ligand (Bi–N 2.510(7) × 2 Å, Bi–O 2.378(7) × 2 Å and Bi–O 2.521(9) × 2 Å) and two S atoms of two thiourea molecules (Bi–S 3.035(4) × 2 Å). Similar to the case of [Bi(Hedta)] [59], in [Bi(Hedta)(tu)$_2$] the "acidic" hydrogen atom of the Hedta^{3-} ligand is not localized on one of the acetate groups, but occupies the center of inversion between two acetate groups of the neighboring complexes, generating a strong hydrogen bond. By means of these hydrogen bonds the [Bi(Hedta)(tu)$_2$] complexes form diagonal chains [92].

In the isostructural complexes K[Bi(edta)(tu)$_2$] [94] and Rb[Bi(edta)(tu)$_2$] [95] Bi(III) has a distorted square antiprismatic environment composed of six donor atoms of edta^{4-} (Bi–N 2.466(2) and 2.481(2) Å, Bi–O 2.362(2)–2.483(2) Å, Table 4) and two S atoms of two thiourea molecules (Bi–S 3.0909(7) and 3.2256(8) Å). A similar structure of the complex anion was established for Cs[Bi(edta)(tu)$_2$]·3H$_2$O [95], but the latter contains two crystallographically independent Bi atoms. In contrast, the lithium complex, Li[Bi(edta)(tu)$_2$]·5.5H$_2$O [93], contains an anionic moiety [Bi(edta)(tu)$_2$–Li(H$_2$O)$_2$–Bi(edta)(tu)$_2$]$^-$, where Li(H$_2$O)$_2{}^+$ cations join two [Bi(edta)(tu)$_2$]$^-$ anions by means of the carbonyl oxygen of the bridging carboxylate groups.

Structures of two mixed ligand Bi–edta complexes with thiourea containing aminoguanidium as cations have also been reported [96]. Figs. 12 and 13 show the structures of the complex anions in (CH$_7$N$_4$)[Bi(edta)(tu)$_2$]·2.5H$_2$O and (CH$_7$N$_4$)[Bi(edta)(tu)(H$_2$O)]·2H$_2$O, respectively. In contrast to the former complex, that has a typical structure of the complex anion [Bi(edta)(tu)$_2$]$^-$ (Bi–N 2.476(1) and 2.529(1) Å, Bi–O 2.379(1)–2.546(1) Å, Bi–S 3.0110(5) and 3.1044(5) Å), the latter complex contains an unusual complex anion [Bi(edta)(tu)(H$_2$O)]$^-$ with three different ligands coordinated to Bi. (CH$_7$N$_4$)[Bi(edta)(tu)(H$_2$O)]·2H$_2$O is the only Bi(III) mixed-ligand complex known to contain in addition to the aminopolycarboxylate anion, two neutral ligands, namely tu and a water molecule.

In spite of evidence of the existence of multiple mixed-ligand ethylenediaminetetraacetatobismuthates(III) with acido-ligands in solution [41,90], in solid state the structures of only three complexes have been reported: (CH$_7$N$_4$)$_2$[Bi(edta)Cl] [97], [Co(NH$_3$)$_5$(NCS)]$_2$[(edta)Bi(μ-C$_2$O$_4$)Bi(edta)]·12H$_2$O [98], and [NdBi(edta)(NO$_3$)$_2$(H$_2$O)$_{7.22}$]$_n$ [99].

(CH$_7$N$_4$)$_2$[Bi(edta)Cl] crystallizes from aqueous solutions containing aminoguanidinium(I) chloride and [Bi(Hedta)]·2H$_2$O in a large range of molar ratios, from 1:1 to 5:1. Interestingly, using alkali metal chlorides or guanidinium chlorides

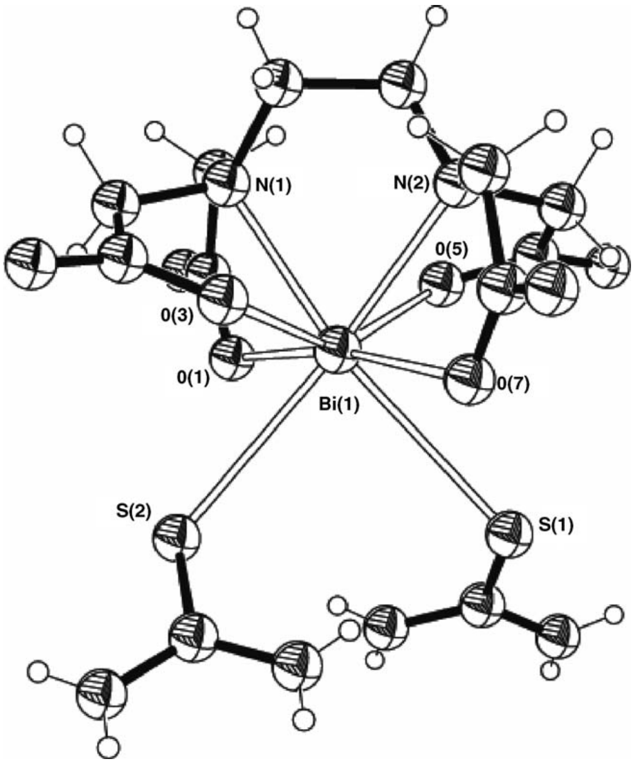


Fig. 12. ADE drawing of the complex anion $[Bi(edta)(tu)_2]^-$ in $(CH_7N_4)[Bi(edta)(tu)_2]\cdot 2.5H_2O$.

does not result in crystallization of analogous mixed-ligand complexes. While heating $(CH_7N_4)_2[Bi(edta)Cl]$ at 150 °C for 1 h no mass loss was noticed. The thermal decomposition begins near 290 °C and results, at 700 °C, in the formation of pure Bi_2O_3.

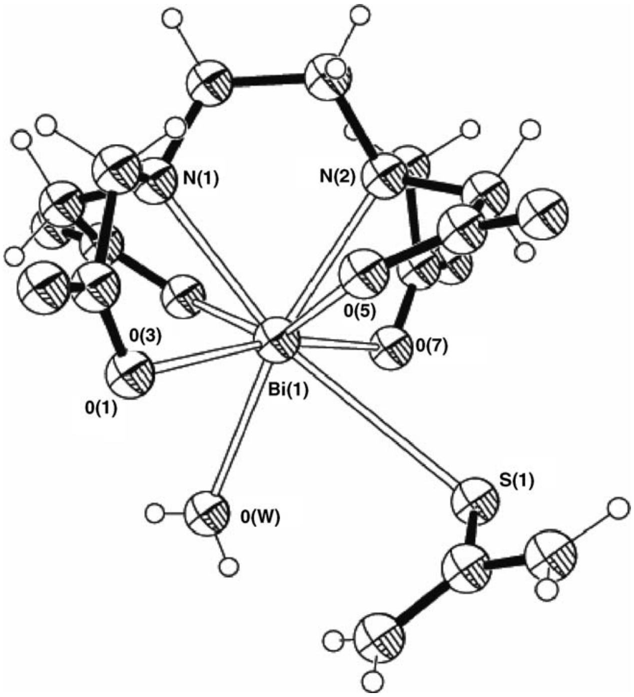


Fig. 13. ADE drawing of the complex anion $[Bi(edta)(tu)(H_2O)]^-$ in $(CH_7N_4)[Bi(edta)(tu)(H_2O)]\cdot 2H_2O$.

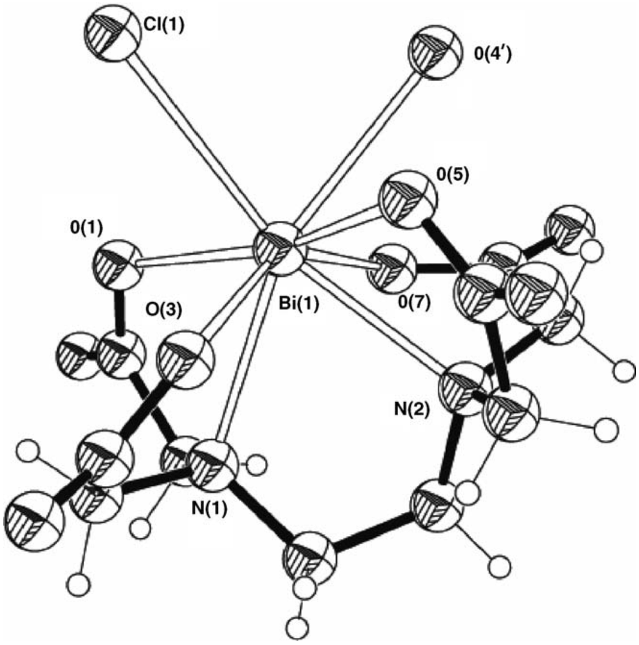


Fig. 14. ADE representation the coordination environment of Bi atom in $(CH_7N_4)_2[Bi(edta)Cl]$.

A distorted square antiprismatic environment can be assigned for bismuth(III), composed of six donor atoms of $edta^{4-}$ ligand (Bi–N 2.465(2) and 2.530(2) Å, Bi–O 2.330(1)–2.524(1) Å), a chloride atom (Bi–Cl 2.9216(6) Å), and the bridging O(4)′ carbonyl atom of the neighboring complex (Bi–O(4)′ 2.707(1) Å) (Fig. 14), that generates polymeric anionic chains [97]. The Bi–Cl bond is longer than the average bond in hexachlorobismuthates(III), containing octahedral $[BiCl_6]^{3-}$ ions, that constitutes 2.70 Å, and is comparable to bridging Bi–Cl bonds in the structures of corresponding dimeric and polymeric chlorobismuthates(III) [100].

Another mixed-ligand complex $[Co(NH_3)_5(NCS)]_2[(edta)Bi(\mu\text{-}C_2O_4)Bi(edta)]\cdot 12H_2O$, was isolated from an aqueous solution containing $[Co(NH_3)_5(NCS)]^{2+}$ and $[Bi(edta)]^-$ ions in the presence of potassium oxalate [98]. The oxalate ion assembles two bismuth centers into binuclear centrosymmetric $[(edta)Bi(\mu\text{–}C_2O_4)Bi(edta)]^{4-}$ complex anions (Fig. 15). The coordination sphere of each Bi atoms includes donor atoms of a hexadentate $edta^{4-}$ chelate ligand (Bi–N 2.520(6) and 2.540(7) Å, Bi–O 2.328(6)–2.598(6) Å) and O atoms of a bridging oxalate ligand (Bi–O 2.523(6) and 2.545(6) Å). The complex anion and the cation are spaced by a Bi–S contact of 3.571 Å.

A heterometallic coordination polymer $[NdBi(edta)(NO_3)_2(H_2O)_{7.22}]_n$ [99], was obtained by reaction of neodymium(III) nitrate and ammonium ethylenediaminetetraacetatobismuthate(III) in aqueous solution. In the crystal structure one of the two NO_3^- anions is disordered in two resolvable positions with 0.74:0.26 occupancy factors. The major component can be formulated as $[(H_2O)_5Nd(\mu_4\text{-}edta)Bi(NO_3)_2]\cdot 3H_2O$, while the minor component was described as $[(NO_3)(H_2O)_3Nd(\mu_4\text{-}edta)Bi(NO_3)]\cdot 2H_2O$. In both cases $edta^{4-}$ acts as a hexadentate ligand toward the Bi atom and monodentate ligand towards the four Nd atoms using

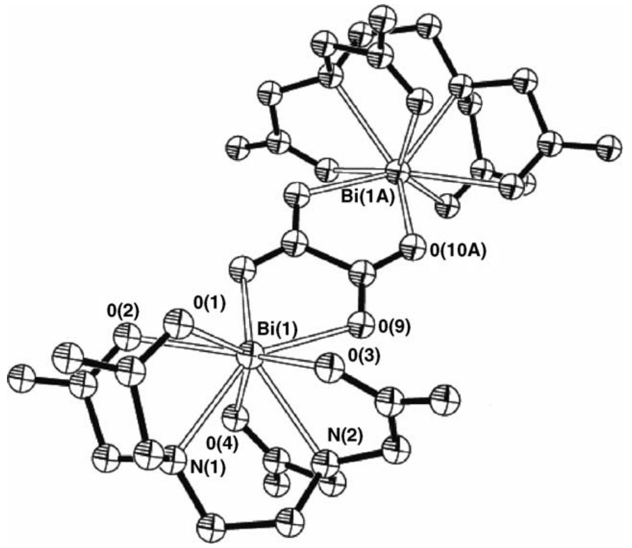


Fig. 15. ADE representation the structure of the complex anion in $[Co(NH_3)_5(NCS)]_2[(edta)Bi(\mu\text{-}C_2O_4)Bi(edta)]\cdot 12H_2O$.

all the 10 donors in coordination. To our best knowledge, this is the only evidence of such structural function for diaminepolycarboxylate ligands. In the former complex, the CN of Bi is 9 + 1 and is achieved by one $edta^{4-}$ ligand and two nitrate groups. In the latter complex, one nitrate group substitutes two water molecules in the coordination polyhedron of Nd and, consequently, the CN of Bi decreases to 7 + 1. The ^1H NMR spectrum of this complex in D_2O shows a singlet at δ 3.63 ppm, assigned to the NCH_2CH_2N group, while the acetate methylene protons gave rise to an AB quartet system ($J_{AB} = 16.60$ Hz) in the range 4.11–4.27 ppm. Thermolysis of the complex occurs in several stages: dehydration in the range 60–170 °C, pyrolysis of the ligands with a single sharp weight loss at 210–260 °C, and the formation of inorganic residue that is completed at 530–550 °C [99].

3.2. *Bi(III) complexes with other than edta^{4-} diaminopolycarboxylate ligands*

Bismuth(III) complexes with other than $edta^{4-}$ diaminopolycarboxylate ligands have been much less studied than corresponding Bi(III)–edta complexes.

The stability constant of the Bi(III) complex with anions of *N*,*N*-hydrazinediacetic acid (H_2hzda) was reported to be 12.50 [101]. Ethylenediamine-*N*,*N*′-diacetic acid (H_2edda) forms a more stable complex with bismuth(III), $\log K = 18.20 \pm 0.03$ [102]. The complexation reaction of Bi(III) with *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid (H_4hedta) has been studied spectrophotometrically [103]. The acid was proposed for use in the UV spectrophotometric determination of Bi(III) at 360 nm [104]. The selectivity of the determination is reported to be higher than that of H_4edta or 1,2-diaminocyclohexanetetraacetic acid (H_4cdta).

Bhat et al. [105] isolated two 1:1 bismuth(III) complexes with $Hhedta^{3-}$ in the solid state. The complex $[Bi(Hhedta)]\cdot H_2O$ was obtained by refluxing Bi_2O_3 with the free acid. Devillers et al. [106] reported synthesis of $[Bi(Hhedta)]\cdot 1.5H_2O$ by reaction of $(BiO)_2CO_3$ and H_4hedta. A highly water soluble sodium salt formulated as $NaBi(hedta)\cdot 4H_2O$ was prepared by reaction of equimolar quantities of $[Bi(Hhedta)]\cdot H_2O$ and 0.1 M aqueous sodium hydroxide [105]. X-ray powder diffraction data and IR spectra of $[Bi(Hhedta)]\cdot H_2O$, and $NaBi(hedta)\cdot 4H_2O$ were reported [51,105]. TGA analysis of $[Bi(Hhedta)]\cdot 1.5H_2O$ revealed that dehydration occurs in the thermal interval 70–160 °C, followed by ligand pyrolysis from about 250 to 290 °C. The third step occurs between 500 and 570 °C and corresponds to the decomposition of carbonate species into bismuth(III) oxide [106].

The reaction of Bi^{3+} with propylenediaminetetraacetic acid (H_4pdta) has been investigated spectrophotometrically and the stability of the complex was determined [107]. The same method was used to determine the composition and the stability constant of the Bi(III) complex with *O*,*O*′-bis(β-aminoethyl)ethylene glycol-*N*,*N*′-tetraacetic acid (H_4egta). The reported stability constants range from $10^{23.77}$ to $10^{25.04}$ [108,109].

1,2-Cyclohexanediaminetetraacetic acid (H_4cdta) forms complexes of high stability with Bi(III). Different authors provide various values for log *K* of $[Bi(cdta)]^-$ complex, from 23.79 [108] to 31.2 [110] or 31.9 [13], however the former value does not seem reliable. Spectrophotometric investigation of the Bi^{3+} complexation with H_4cdta showed the formation at low pH (pH 0.1–0.5) of [Bi(Hcdta)] ($\log K = 19.11$); between pH 1.5 and 10 $[Bi(cdta)]^-$ exists ($\log K = 27.21$), while at pH higher than 10, hydrolysis begins [52].

The acidic complex $[Bi(Hcdta)]\cdot 5H_2O$ was isolated and characterized by Devillers and co-workers [111]. It was obtained by refluxing 1,2-cyclohexanediaminetetraacetic acid and $(BiO)_2CO_3$ in water. The compound crystallizes as a pentahydrate, but after several hours in vacuum it generates $[Bi(Hcdta)]\cdot H_2O$. TGA of the monohydrate showed that the water molecule is removed between 80 and 140 °C, followed by ligand pyrolysis (305–330 °C) and formation of the bismuth(III) oxide (490–540 °C) [106].

In the crystal structure of $[Bi(Hcdta)]\cdot 5H_2O$ there are two crystallographically independent [Bi(Hcdta)] molecules. The Bi atom is surrounded by eight donor atoms of the ligand in a square antiprismatic environment. $(Hcdta)^-$ anion acts as a hexadentate ligand towards one Bi atom, the remaining two coordination positions being occupied by two O atoms of the neighboring complexes. Two acetate groups of $Hcdta^-$ are monodentate, while the other two act as bridging groups, generating dimers. Centrosymmetric dimers formed by Bi(1) and Bi(2) are bridged by oxygen atoms and form polymeric ribbons.

$Cs[Bi(cdta)]\cdot 5.5H_2O$ has been prepared by reacting $(BiO)_2CO_3$, $H_4cdta\cdot H_2O$ and CsOH [112]. The square antiprismatic coordination environment of Bi is composed of six $cdta^{4-}$ donor atoms and two oxygen atoms from carboxylate groups of the neighboring complexes, generating centrosymmetric dimers connected in polymeric ribbons (Fig. 16). The polymeric ribbons in the structures of $Cs[Bi(cdta)]\cdot 5.5H_2O$ and $[Bi(Hcdta)]\cdot 5H_2O$ are similar, but the structure of the centrosymmetric dimers in these compounds is quite different. In the structure of $[Bi(Hcdta)]\cdot 5H_2O$, the centrosymmetric dimers of

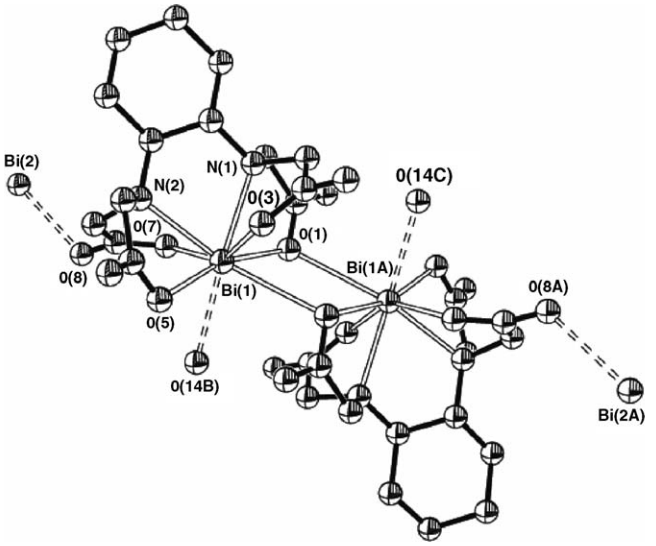


Fig. 16. ADE drawing of fragment of polymeric ribbon in $Cs[Bi(cdta)]\cdot5.5H_2O$ structure.

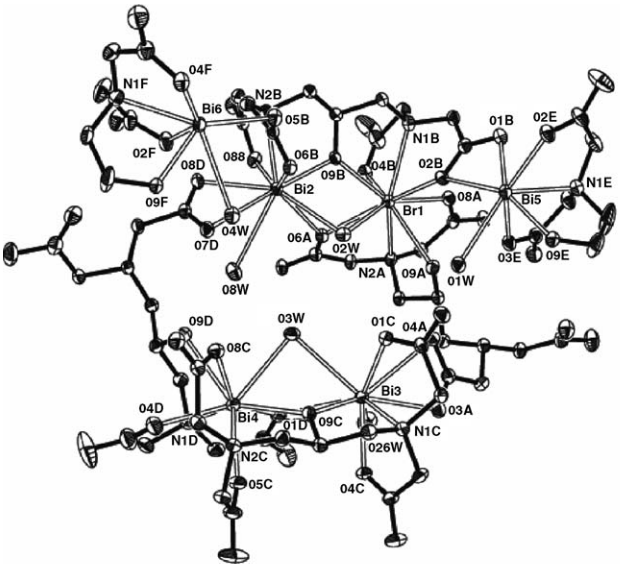


Fig. 17. ADE drawing of one asymmetric part of the $[Bi_{12}(H_2hpdta)_4(Hhpdta)_6(H_2O)_{12}]\cdot80H_2O$ structure.

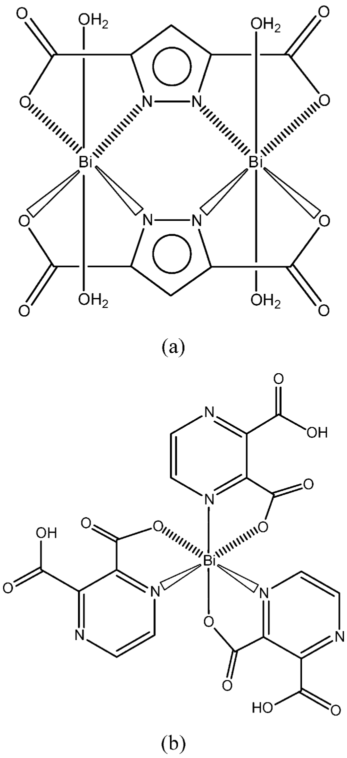
the Bi(1) and Bi(2) atoms involve only the carbonyl oxygen atoms of the neighboring complexes, while in the structure of $Cs[Bi(cdta)]\cdot5.5H_2O$, the dimer of the Bi(1) atoms is formed by chelate-forming oxygen atoms, whereas the dimer of the Bi(2) atoms, like that of the corresponding Bi(1) atoms in the structure of $[Bi(Hcdta)]\cdot5H_2O$, is formed with the participation of the carbonyl oxygen atoms of the neighboring complexes. The Bi–N bond distances in the structure of $Cs[Bi(cdta)]\cdot5.5H_2O$ are within 2.469(3)–2.501 Å. The Bi–O chelate bonds for the two independent Bi atoms are in the range 2.328(3)–2.504(4) Å, while the distances from Bi atoms to the bridging oxygen atoms are in the range from 2.612(9) to 2.916(9) Å. It should be noted that in the first independent $[Bi(cdta)]^-$ complex two out of four acetate groups are bridging, while in the second one only one is bridging.

2-Hydroxy-1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_5hpdta) is interesting because of the presence of the hydroxyl group that can participate in metal coordination. The complexation of Bi(III) with H_5hpdta was studied spectrophotometrically and the stability constants were reported [113]. Devillers and co-workers [114] have recently reported the synthesis and structure of a dodecanuclear Bi(III) complex with H_5hpdta $[Bi_{12}(H_2hpdta)_4(Hhpdta)_6(H_2O)_{12}]\cdot80H_2O$. The only other known dodecanuclear Bi(III) complex is the oxo-citrato cluster in $(NH_4)_{12}[Bi_{12}O_8(cit)_8]\cdot10H_2O$, reported by Asato et al. [115]. $[Bi_{12}(H_2hpdta)_4(Hhpdta)_6(H_2O)_{12}]\cdot80H_2O$ has a different structure and was synthesized by reaction of bismuth(III) oxocarbonate and H_5hpdta. In its crystal structure two asymmetric parts each contain six bismuth atoms in a nine-fold coordination environment (Fig. 17). The coordination polyhedra can be described as a monocapped square antiprism or a tricapped trigonal prism, both slightly distorted. This is a unique example of bismuth PAPC complex; each ligand coordinates several metal centers. The bond distances are in a wide range, from 2.19 to 3.22 Å. Bismuth centers are bridged either by two or three oxygen atoms at the same time. The particularities of this structure were explained by involvement of the central hydroxo-group in Bi coordination.

The same group of authors reported the synthesis of a 1:1 Bi(III)–hpdta complex, formulated in [106] as $Bi(H_2hpdta)\cdot2H_2O$. When heated in air, the complex loses water molecules between 70 and 240 °C. Thermal decomposition takes place in two steps, at 240–280 and 280–300 °C. The final decomposition temperature is 475 °C and results in formation of Bi_2O_3.

Bismuth(III) complexes with anions of heteroaromatic diaminodicarboxylic acids are also known. Bismuth 3,5-pyrazoledicarboxylate $Bi_2(3,5\text{-dcp})_2\cdot4H_2O$, is obtained in 89% yield from the reaction of a nitric acid solution of $Bi(NO_3)_3$ with 3,5-pyrazoledicarboxylic acid in hot water [116]. The IR and XPS spectra support the formation of trianionic bridging 3,5-dcp^{3-} species. Complexation of Bi(III) by one nitrogen was responsible for the enhanced acidity of the neighboring pyrazolic hydrogen atom. The authors proposed a binuclear structure with a CN 6 for each Bi(III) atom (Chart 1(a)) but taking into account the low solubility of this compound and the tendency of Bi(III) to form carboxylate bridges, the structure may be polymeric, and the actual CN may be probably higher.

The reaction of Bi_2O_3 with pyrazine-2,3-dicarboxylic acid (H_2pzdc) produces a solid, which has a very low solubility in common organic solvents. Postel and co-workers [47] suggested a $\{Bi(pzdc)(OH)\}_n$ stoichiometry for this product, mainly based on IR data. Later, Devillers and co-workers [116] obtained the same compound by reacting nitric acid solutions of $Bi(NO_3)_3$ with the corresponding acid in 1:1.5 ratio, but found the actual stoichiometry was different, $\{Bi(2,3\text{-}Hpzdc)_2OH\}$, as supported by elemental analysis. However, when a 1:3 ratio of the reagents is used, the product is $Bi(2,3\text{-}Hpzdc)_3\cdot2H_2O$ [116]. The existence of protonated carboxylic groups is supported by the presence of a strong band at



(a)

(b)

Chart 1. Proposed structures for $Bi_2(3,5\text{-dcp})_2{\cdot}4H_2O$ (a) and $Bi(2,3\text{-Hpzdc})_3{\cdot}2H_2O$ (b) [116].

1723 cm^{-1} in the IR spectrum, attributable to the carboxyl group stretching vibrations, correlated with the broad signal at 13.24 ppm in the ^1H NMR spectrum. The proposed structure of this complex is presented in Chart 1(b), but again, the actual CN of Bi(III) may be probably higher than 6. When heated in air or nitrogen both $Bi(2,3\text{-Hpzdc})_3{\cdot}2H_2O$ and $Bi_2(3,5\text{-dcp})_2{\cdot}4H_2O$ are converted into α-Bi_2O_3 at moderate temperatures (451 and 385 °C, respectively). These complexes were proposed as precursors for bismuth-based oxides. No Bi(III) pyrazine- or pyrazole-dicarboxylates have been structurally characterized.

4. Bismuth complexes with polyaminopolycarboxylate ligands

4.1. Bi(III) complexes with diethylenetriaminepentaacetate ligands and its analogues

Bi(III) forms stable complexes with the anions of diethylenetriaminepentaacetic acid (H_5dtpa); however, the reported stability constants are quite different. For example the determined log K of $[Bi(dtpa)]^{2-}$ in [117] is 30.30, while in [8] is 35.60. Spectrophotometric investigation of the complexation reaction of Bi(III) and H_5dtpa showed the formation of 1:1 complexes with different protonations. In highly acidic solutions $[Bi(H_2dtpa)]$ exists $\{\log K\ [Bi(H_2dtpa)] = 16.80\}$, while between 0.6–2.0 and 2.1–2.6 formation of the monoprotonated $(\{\log K\ [Bi(Hdtpa)]^- = 23.02\})$ and the completely deprotonated $(\{\log K\, [Bi(dtpa)]^{2-} = 31.65\})$ species occurs. Kornev and Trubachev [26] reported for the log K of $[Bi(dtpa)]^{2-}$ a value of 29.29. The acid H_5dtpa was proposed for the spectrophotometric determination of Bi at 270 nm [118].

In the solid state the first $[Bi(H_2dtpa)]{\cdot}H_2O$ complex was obtained by Krishna Iyer and Shankar [57]. Later, Martynenko and co-workers [119] reported the synthesis of Bi(III)–dtpa complexes, namely $[Bi(H_2dtpa)]{\cdot}2H_2O$, $K_2Bi(dtpa){\cdot}4H_2O$, $CuBi(dtpa){\cdot}5H_2O$, and $Bi_5(dtpa)_3{\cdot}10H_2O$.

A series of heterometallic complexes, $M^{II}Bi(dtpa){\cdot}nH_2O$ (M^{II} = Co(II), Ni(II), Cu(II) [66]; or Pb(II) [120]), were synthesized and characterized by elemental analysis and spectroscopic techniques. Investigation of the full decomposition process with high temperature X-ray diffraction (HTXRD) and TGA shows the occurrence of three consecutive steps: dehydration, ligand pyrolysis and the formation of inorganic residues. Pyrolysis of $PbBi(dtpa){\cdot}3H_2O$ yielded a mixture of PbO and an unknown phase, which could not be identified according to the PbO–Bi_2O_3 phase diagram [120].

Bulimestru et al. [121] synthesized and characterized a heterometallic Co(III)–Bi(III)–dtpa complex $[Co(tsc)_3]_2[Bi(dtpa)]_2SO_4{\cdot}10H_2O$ (tsc, thiosemicarbazide). The complex contains $[Co(tsc)_3]^{3+}$ cations, $[Bi(dtpa)]^{2-}$ anions, and lattice water molecules. In the complex cation $[Co(tsc)_3]^{3+}$, Co(III) has a *fac*-configuration, while the complex anion has bismuth coordinated to three N-donors and five O-donors of $dtpa^{5-}$, generating a distorted bicapped trigonal prism.

X-ray study of $[Bi(H_2dtpa)]{\cdot}2H_2O$ [122] showed the H_2dtpa^{3-} ligand coordinating in a heptadentate fashion to one Bi atom by means of its three nitrogen donors, three oxygen atoms of the deprotonated carboxylic groups, and the carbonyl oxygen atom of one protonated carboxylic group. In addition, the Bi atom forms a bridging bond with a carbonylic oxygen atom of the neighboring complex. The coordination polyhedron around the Bi atom is intermediate between a square antiprism and bicapped trigonal prism. The Bi–N and Bi–O bonds in $[Bi(H_2dtpa)]{\cdot}2H_2O$ are in the range 2.449(3)–2.723(4) Å and 2.290(3)–2.699(3) Å, respectively. Interestingly, the bridging bond Bi–O(2) is shorter than one of the chelate Bi–O bonds. By means of the Bi–O(2) bridging bond, the $[Bi(H_2dtpa)]{\cdot}2H_2O$ complexes form polymeric chains.

Interaction of $Bi(H_2dtpa){\cdot}2H_2O$ and ammonium or alkali metal carbonates in equivalent quantities led to the formation of the compounds $M[Bi(Hdtpa)]{\cdot}5H_2O$ ($M^+ = Na^+, K^+, Rb^+$, and NH_4^+). The crystal structure of the potassium salt was reported and was found to consist of K^+ cations $[Bi(Hdtpa)(H_2O)]^-$ anions (Fig. 18) and water molecules [123]. Nine-coordination geometry of Bi in the complex anion is imposed by three nitrogen donors (Bi–N 2.489(7)–2.669(2) Å), four oxygen atoms of deprotonated acetate groups (Bi–O 2.362(8)–2.568(8) Å), the carbonyl oxygen atom of the protonated carboxylate group (2.734(8) Å), and the oxygen atom of a coordinated water molecule (Bi–O_w 2.749(8) Å).

Reaction of bismuth oxocarbonate with H_5dtpa with subsequent neutralization of the resulting solution with guanidinium carbonate gives $(CH_6N_3)_2Bi(dtpa){\cdot}4H_2O$ [29]. In [106] this complex was formulated as $(CH_6N_3)_2Bi(dtpa){\cdot}2H_2O$. TGA

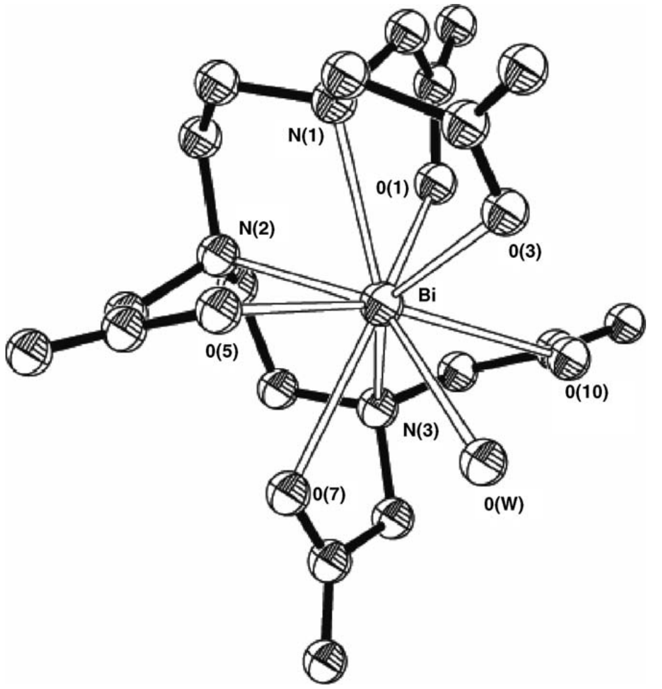


Fig. 18. ADE representation the structure of the complex anion in K[Bi(Hdtpa)(H_2O)]·$4H_2O$.

shows that dehydration occurs between 80 and 125 °C followed by several steps of ligand pyrolysis between 290 and 450 °C, with the formation of Bi_2O_3 at 480 °C.

In the crystal structure of $(CH_6N_3)_2$[Bi(dtpa)]·$4H_2O$ [29] Bi(III) has a nine-coordination environment; the ninth coordination site is occupied by a carbonyl oxygen atom of the neighboring complex, generating dimers. The Bi–N bond lengths are in the range 2.536(7)–2.639(6) Å, Bi–O distances vary between 2.368(5) and 2.599(5) Å, while the distance from the Bi atom to the bridging oxygen atom is 2.686(6) Å.

Brechbiel and co-workers [122] reported an improved synthesis of a more preorganized analogue of H_5dtpa, *N*-(2-aminoethyl)-*trans*-1,2-diaminocyclohexane-*N*,*N*′,*N*″-pentaacetic acid (H_5cdtpa) and obtained a Bi(III) complex $(CN_3H_6)_2$[Bi(cdtpa)]. The Bi–N distances in this compound range from 2.458(5) to 2.592(5) Å, while Bi–O bonds are in the range 2.371(4)–2.610(4) Å. The coordination polyhedron of the Bi atoms lies along a D_2-symmetric interconversion pathway between a square antiprism and a dodecahedron.

The crystal structure of a Bi complex with dtpa derivative, udtpa–[Bi(udtpa)(H_2O)]·$8.5H_2O$ (udtpa = dtpa–bis(4,5-diamino-6-hydroxy-2-mercaptopyrimidine)) is reported [124]. The geometry of the bismuth coordination polyhedron can be described as monocapped-square antiprismatic and comprises eight donors of the octadentate chelating ligand (3N + 5O) and the ninth site occupied by an aqua ligand (Fig. 19). The Bi–O coordination distances are in the range 2.337–2.784 Å (the longest bond is Bi–O_w), while Bi–N bonds are in the range 2.440–2.617 Å.

As in the case of K[Bi(Hdtpa)(H_2O)]·$4H_2O$, a water molecule completes the ninth coordination site of Bi(III). It seems that while good ligands for Bi(III), octadentate dtpa-type ligands cannot always satisfy the coordination requirements of this cation, and in solid state both nine- and eight-coordinate Bi(III) have been found. Although the number of structurally characterized Bi(III)–dtpa-type complexes is still limited, there is definitely an effect of the "counter cation", showing yet again that the primary coordination sphere of Bi(III) is not independent of the nature of the secondary.

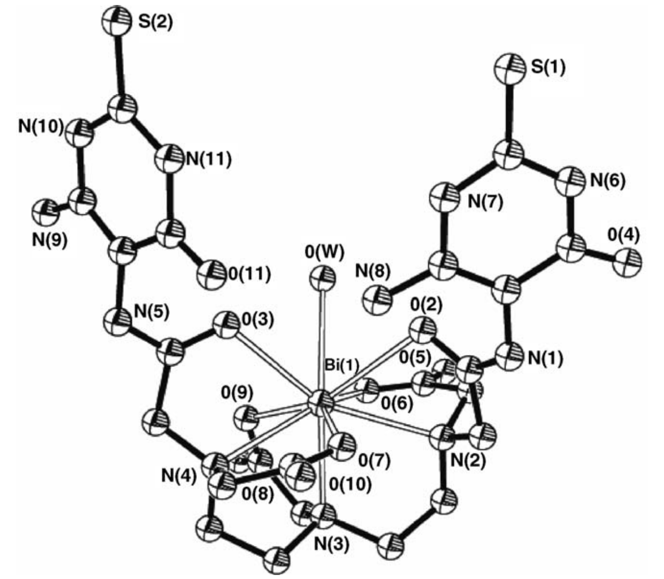


Fig. 19. ADE representation the structure of [Bi(udtpa)(H_2O)] complex in [Bi(udtpa)(H_2O)]·$8.5H_2O$.

4.2. Bi(III) complexes with triethylenetetraaminehexaacetate ligands

Anions of triethylenetetraaminehexaacetic acid (H_6ttha) potentially can be decadentate ligands and can form both mononuclear and binuclear complexes with metal ions. The complexation reaction of Bi(III) with H_6ttha has been studied spectrophotometrically and the stability constant of the protonated 1:1 complex was reported to be 22.59 ± 0.01 [14]. Yingst and Martell [125] studied the potentiometric equilibrium in the Bi(III)–ttha system and suggested the formation of only 1:1 complexes, in contrast with Ln(III) and Ga(III), that can form both 1:1 and 2:1 complexes in aqueous solutions.

In the solid state, however, both 1:1 and 2:1 Bi(III)–H_6ttha complexes have been isolated: [Bi(H_3ttha)]·$2.5H_2O$ and Bi_2(ttha)·$3.5H_2O$, respectively [106,126]. Two Ln–Bi heterobimetallic H_6ttha complexes, LaBi(ttha) and PrBi(ttha) were synthesized and proved to be useful precursors for Bi–Ln mixed oxide systems. The TGA investigation of the mono and heterometallic Bi–ttha complexes showed the occurrence of three successive steps, corresponding to dehydration, ligand pyrolysis and the final evolution of CO_2 leading to the oxide or mixed-oxide system. Dehydration starts at 60–85 °C and ends between 120 and 190 °C. The ligand pyrolysis starts around 270–280 °C resulting in carbonate-type compounds. The final decomposition temperatures range between 375 and 570 °C, while the final pyrolysis products are Bi_2O_3 in the case of monometal-

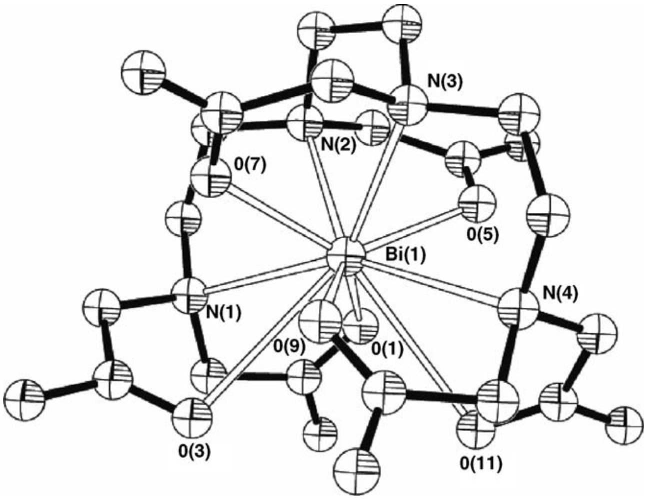


Fig. 20. ADE drawing of Bi(1) unit in $[Bi(H_3ttha)]\cdot 3H_2O$.

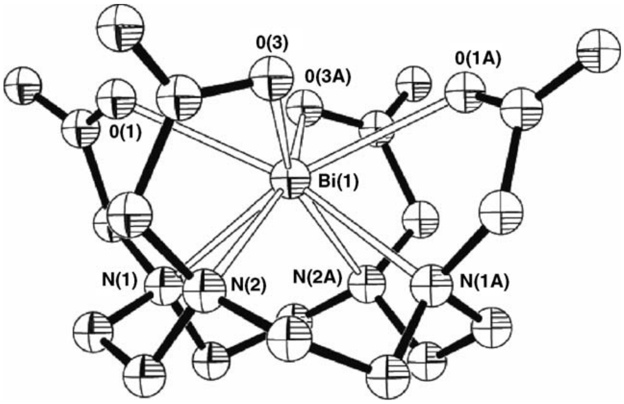


Fig. 21. ADE representation of the Bi environment in $Na[Bi(dota)]\cdot H_2O$.

lic complexes or $BiLaO_3$ and $BiPr^{III}{}_{1-x}Pr^{IV}{}_xO_{3+0,5x}$ in the case of corresponding Bi–Ln heterodimetallic complexes [106,126].

Crystal structures of two Bi–ttha complexes are reported: $[Bi(H_3ttha)]\cdot 3H_2O$ [111] and $(CH_6N_3)_2[Bi(Httha)]\cdot 4H_2O$ [127]. It seemed plausible that increasing the number of donor atoms of the ligand would increase the CN of Bi(III). Indeed, in both of the two crystallographically independent $[Bi(H_3ttha)]$ (Fig. 20) complexes of $[Bi(H_3ttha)]\cdot 3H_2O$, Bi(III) has a CN = 10, and its coordination polyhedron may be best described as a bicapped square antiprism. The H_3ttha^{3-} ligand is decadentate, using for coordination its four nitrogen and six oxygen donors. The Bi–O distances in the two complexes, 1A and 1B, vary from 2.320(7) to 3.058(8) Å for the former, and from 2.327(7) to 2.988(8) Å for the latter, while the Bi–N bonds in both complexes are identical (respectively 2.473(9) × 2, 2.813(8) × 2, 2.472(9) × 2, and 2.803(9) × 2 Å). The main difference between the complexes 1A and 1B is the length of Bi–O(1) bond, 2.694(7) versus 2.912(7) Å.

In contrast, in $(CH_6N_3)_2[Bi(Httha)]\cdot 4H_2O$ [127], the bismuth atom adopts a nine-coordinate environment formed by four nitrogen and five oxygen atoms of the $Httha^{5-}$ ligand. The protonated carboxylic group does not participate in coordination, the corresponding C–O bonds are quite indicative of this (1.18 Å for C=O, and 1.32 Å for C–OH bond). The coordination polyhedron in $(CH_6N_3)_2[Bi(Httha)]\cdot 4H_2O$ can be best described as a monocapped square antiprism. The Bi–O bond lengths vary from 2.327(6) to 2.560(6) Å, while Bi–N bonds are very similar, from 2.619(7) to 2.688(8) Å. It should be noted that the hydrogen atom of the protonated carboxylic group H(1 0 1) is involved in a very strong hydrogen bond with the oxygen atom O(1 0 2) of the symmetric complex, generating pseudo dimers.

4.3. Bi(III) complexes with macrocyclic polyaminopolycarboxylate ligands

Complexes of bismuth with anions of macrocyclic polyaminopolycarboxylic acids were shown to be kinetically inert [128]. Bismuth complexes with anions of H_3nota, H_4dota, H_4teta were isolated in solid state as white powders. Their aqueous solutions show UV spectra absorption bands at 285, 305, and 323 nm, respectively.

Complexes of Bi(III) with two cyclen derivatives were reported, $NaBi(dota)\cdot H_2O$ and Bi(do3a–Bu), where H_4dota = 1,4,7,10-tetraazacyclododecane–1,4,7,10-tetraacetic acid and H_3do3a–Bu = 10-[2,3-dihydroxy-(1-hydroxymethyl) propyl]-1,4,7,10-tetraazacyclododecane-1,4,7,-triacetic acid [9]. The stability constants determined with the study of the equilibria between Bi(III) and free acids, are very high, $\log K = 30.3$ for $[Bi(dota)]^-$, and 26.8 for [Bi(do3a–Bu)], respectively.

The X-ray structure of $Na[Bi(dota)]\cdot H_2O$ showed that the ligand coordinated in an octadentate fashion (Fig. 21). The Bi atom is deeply located in the cage formed by the nitrogen and oxygen donors; this is in accordance with the high thermodynamic stability of the complex. The Bi–O and Bi–N bond distances are very close and differ by less than 0.1 Å (Bi–O 2.495–2.580 and Bi–N 2.516–2.535 Å). The mean Bi–N bond length is 2.526(2) Å, similar to those observed in $[Na(H_2O)_4][Bi(H_4dotmp)]$ [129], in which Bi(III) also adopts an octa-fold coordination environment.

The temperature dependent ^1H and ^{13}C NMR spectra indicate that both complexes are fluxional. The $[Bi(dota)]^-$ complex shows a C_{4v} symmetry in solution, which is very similar to that found in solid state. The methylene protons of coordinated acetate groups give an AB doublet with a large coupling $^2J_{HH}$ constant, 17.85 Hz. The reason for such a large $^2J_{HH}$ is thought to be the strong coordination of acetate groups that stabilize the conformation with a planar chelate ring; this is supported by X-ray data. The ^{13}C spectrum of $[Bi(dota)]^-$ exhibits one signal for quaternary carbon atoms of four magnetically equivalent carboxylate groups at 179.1 ppm. The signal of the methylene carbon of acetate groups appear at 55.0 ppm, while the CH_2 carbon atoms of cyclen ring give rise to two signals, at 55.0 and 50.5 ppm. No diastereoisomerism was detected and this fact was associated with the size of Bi^{3+}. The observed fluxional motion was attributed to the exchange process in the helicity of the enantiomer pair $\Delta(\delta\delta\delta\delta) \leftrightarrow \Lambda(\lambda\lambda\lambda\lambda)$. Based on the activation parameters, a synchronous process was suggested for the motion of the ring and the acetate arms. NMR studies showed that the

OH group attached to the middle carbon of the "butriol" side chain in [Bi(do3a–Bu)] is coordinated to Bi(III). At pH 8.73 the coordinated OH group is predominantly deprotonated. From the ^{1}H NMR spectrum, it was concluded that [Bi(do3a–Bu)] probably exhibits the same fluxional properties as the $[Bi(dota)]^-$ complex [9].

The structural data for bismuth(III) complexes with anions of polyaminopolycarboxylic acids are summarized in Table 5.

5. Generalities

Bismuth(III) forms stable complexes with a large number of aminopolycarboxylate and polyamino-polycarboxylate ligands that can be isolated in solid state. Bismuth(III) usually exhibits CN 8, with a few examples of 7, 9 or 10 coordination. Increasing the number of donor atoms of the ligand is usually accompanied by a change in structure from polymeric to monomeric, but does not necessarily involve an increase in CN of Bi. The coordination environment of bismuth is labile and can involve one water molecule, various neutral or acido-ligands, as well as oxygen atoms of the carboxylate groups of the neighboring Bi(III) complexes, in addition to coordination via aminopolycarboxylate or polyaminopolycarboxylate ligands. Monomers, dimers or polymeric arrays can be generated.

Some general comments can be made regarding the participation of the carboxylate groups in the formation of binuclear or polynuclear species. The analysis of the structural data presented in Tables 2–5 shows four types of carboxylate bridges (Scheme 1). In types 1 and 2, the carboxylate groups exhibit bidentate bridging functions (η^1:η^1:μ_2). Usually the Bi–O bonds are quite asymmetric, with the differences between Bi–O distances often exceeding 10%. Type 3 is common for some dimeric structures, where one oxygen atom of the carboxylate group binds in a bidentate fashion to two metal centers (η^0:η^2:μ_2). Type 4 is characteristic of tridentate bridging carboxylate groups (η^1:η^2:μ_2) with a relative low occurrence in Bi(III) APC and PAPC complexes. In some complexes, several types of bridging carboxylate groups were found in addition to mono- and bidentate non-bridging modes. From this point of view the dodecanuclear complex of Bi(III) with H_5hpdta $[Bi_{12}(H_2hpdta)_4(Hhpdta)_6(H_2O)_{12}]\cdot 80H_2O$ [114], which contains mono-, and bidentate non-bridging carboxylate groups, types 3 and 4 bridging carboxylate groups, as well as some COOH groups not involved in any coordination, is very unusual.

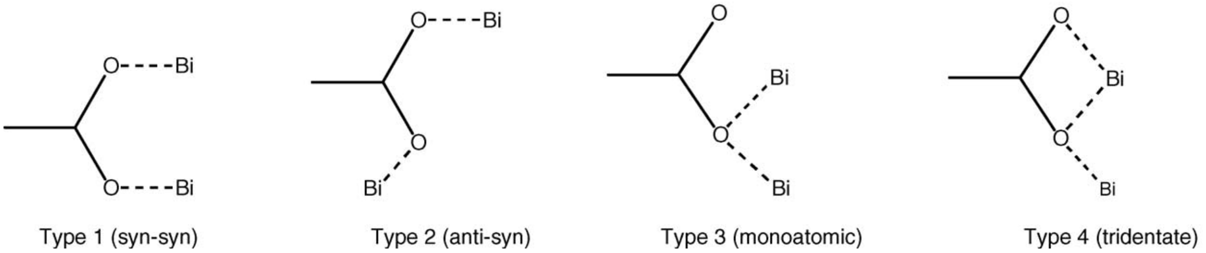
There are a large number of Bi(III) APC and PAPC complexes that contain water molecules coordinated to bismuth(III): $[Bi(nta)(H_2O)_2]$ [29,32], $[Bi(heida)(H_2O)]\cdot H_2O$ [44], $(CH_6N_3)[Bi(edta)(H_2O)]$ [78,79,84], $(CH_6N_3S)[Bi(edta)(H_2O)]$ [82], $(enH_2)[Bi(edta)(H_2O)]_2\cdot 4H_2O$ [80], $(H_3HCH_2CH_2CO_2H)[Bi(edta)(H_2O)]$ [81], $Ba[Bi_2(edta)_2(H_2O)]\cdot H_2O$ [76], $[Co(NH_3)_2(ala)_2][Bi(edta)(H_2O)]\cdot 5H_2O$ [84], $[Co(Hdmg)_2(o\text{-tol})_2][Bi(edta)(H_2O)]\cdot 5H_2O$ [86], $K[Bi(Hdtpa)(H_2O)]\cdot 4H_2O$ [123], and $[Bi(udtpa)(H_2O)]\cdot 8.5H_2O$ [124]. Since these complexes were discussed in previous sections here we will focus on some trends in bismuth–water molecule interactions.

Table 5
Structural features of Bi(III) polyaminopolycarboxylates

Compound	CN, polyhedron	Type of structure	Bond distances (Å)		References
			d(Bi–N)	d(Bi–O)	
$[Bi(H_2dtpa)]\cdot 2H_2O$	8, BTP	Polymeric (chain)	2.449(4), 2.563(4), 2.723(4)	2.290(3), 2.309(3), 2.602(3), 2.699(3), 2.620(3)[a]	[122]
$(CH_6N_3)_2[Bi(dtpa)]\cdot 4H_2O$	9, MSA	Dimeric	2.536(7), 2.626(6), 2.639(6)	2.368(5), 2.479(5), 2.494(5), 2.562(5), 2.599(5), 2.686(6)[a]	[29]
$[Co(tsc)_3]_2[Bi(dtpa)]_2SO_4\cdot 10H_2O$	8, BTP	Monomeric	2.476(7), 2.515(7), 2.638(7)	2.328(5), 2.412(6), 2.561(7), 2.594(6), 2.604(6)	[121]
$K[Bi(Hdtpa)(H_2O)]\cdot 4H_2O$	9, MSA	Monomeric	2.489(7), 2.55(1), 2.669(8)	2.362(8), 2.384(7), 2.525(8), 2.568(8), 2.734(8), 2.749(7)[b]	[123]
$(CH_6N_3)_2[Bi(cdtpa)]$	8, D	Monomeric	2.458(5), 2.548(5), 2.592(5)	2.371(4), 2.405(4), 2.479(4), 2.528(4), 2.610(4)	[122]
$[Bi(udtpa)(H_2O)]\cdot 8.5H_2O$	9, MSA	Monomeric	2.440(7), 2.577(7), 2.617(7)	2.337(6), 2.387(6), 2.475(7), 2.617(7), 2.636(7), 2.78(1)[b]	[124]
$[Bi(H_3ttha)]\cdot 3H_2O$	Bi(1) 10, BSA	Monomeric	2.473(9) × 2, 2.813(8) × 2	2.320(7) × 2, 2.694(7) × 2, 3.055(8) × 2	[111]
	Bi(2) 10, BSA	Monomeric	2.472(8) × 2, 2.803(8) × 2	2.327(7) × 2, 2.912(7) × 2, 2.988(8) × 2	
$(CH_6N_3)_2[Bi(Httha)]\cdot 4H_2O$	9, MSA	Monomeric	2.619(7), 2.649(7), 2.687(6), 2.688(7)	2.327(6), 2.408(6), 2.474(6), 2.554(6), 2.560(6)	[127]
$Na[Bi(dota)]\cdot H_2O$	8, SA	Monomeric	2.516(5) × 2, 2.535(5) × 2	2.495(4) × 2, 2.580(5) × 2	[9]

[a] Bridging Bi–O(carbonylic).

[b] Bi–O(H_2O).


Type 1 (syn-syn) Type 2 (anti-syn) Type 3 (monoatomic) Type 4 (tridentate)

Scheme 1. Carboxylate bridges found in Bi(III) APC and PAPC complexes.

The shortest Bi–O(H_2O) distance in these complexes was observed in [Bi(nta)(H_2O)$_2$] [29,32]. Two groups of authors investigated its structure and reported 2.403(6) and 2.415(8) Å, respectively, for this bond. These values are significantly lower than the average Bi–O(H_2O) distance in bismuth(III) APC and PAPC complexes: 2.71 Å. Interestingly, the second Bi–O(H_2O) bond in this complex is significantly longer, 2.767 Å [29] (the value for this bond reported by the other group was 2.759 Å [32]). In Ba[Bi_2(edta)$_2$(H_2O)]·H_2O [76] the Bi–O(H_2O) distance corresponding to different independent Bi atoms differs, too, but in this case this difference is not as considerable, 2.73 versus 2.66 Å. Another interesting feature is the Bi–O(H_2O) bond in (CH_6N_3S)[Bi(edta)(H_2O)] [82], which is the only known Bi–edta complex with CN = 7. The decrease in CN results in a shorter Bi–O(H_2O) distance, 2.640 Å, in comparison with the average observed value.

Another point of interest was the role of the lone electron pair in the crystal structures of Bi(III) APC and PAPC complexes. The most widely practiced method for describing the stereochemistry of p-element complexes is the valence shell electron pair repulsion model (VSEPR), originally developed in the 1960s, and expanded by Gillespie [130,131]. The basic premise of VSEPR is that pairs of electrons in the valence shell of the central atom of a molecule repel each other and take up positions as far apart as possible.

With regard to the position of Bi in the periodic table of elements, a decrease in the stereochemical role of the lone electron pair of Bi(III) was confirmed for bismuth APC and PAPC complexes [132,133]. The stereochemical effect of the lone electron pair of Bi(III) was estimated by calculating the displacement of Bi(III) atoms from the center of the coordination polyhedron [132] or from the center of the Voronoi–Dirichlet (VD) polyhedra [134]. The average value of the displacement of the Bi atom of the VD polyhedra in diaminopolycarboxylates was reported to be 0.16 Å, corresponding to a weak activity of the lone electron pair. For instance, in the case of Sb(III) this value is much higher (0.4 Å). It was shown that the presence of the lone electron pair is responsible, to a certain extent, for the asymmetry of the bismuth coordination environment in diaminopolycarboxylate complexes, but this effect is less expressed compared to respective antimony complexes [134]. Pb(II) is isoelectronic to Bi(III) and also displays a stereochemically active lone pair of electrons in its APC and PAPC complexes. The stereochemistry of Pb(II) complexes with these ligands and the role of the lone pair of electrons in these compounds have been recently examined in detail [135]. The analysis and comparison of the structural features of Pb(II)/Bi(III) APC and PAPC complexes showed that the Bi(III) compounds display: (i) an increased tendency to exhibit higher CN, and (ii) a greater association between neighboring units through carboxylate bridges.

6. Applications

Bismuth(III) complexes with APC and PAPC ligands have attracted significant interest due to a wide range of applications, from pharmaceuticals to high-tech materials. Nowadays it is commonly accepted that of all heavy metals, bismuth has one of the greatest potential for applications, from medicine to materials. Its compounds are less toxic than those of other heavy metals, and some of them are therapeutically useful [1].

Bismuth isotopes emitting α-particles have been investigated for potential use as radio-therapeutic agents for the treatment of cancer [136–140]. A number of polyaminopolycarboxylate ligands have been considered for bismuth radioisotope chelation. All of these complexes have high thermodynamic stability constants [12,13]. It is not our intention to cover the extensive literature on this topic, but we will mention some recent work and present the kind of ligands considered so far, as well as their advantages and drawbacks. Hassfjell and Brechbiel [20] have recently reviewed the use of promising α-emitting ^{212}Bi ($T_{1/2} = 60$ min), and ^{213}Bi ($T_{1/2} = 47$ min). These nuclei offer some advantages over other radiopharmaceuticals as they are relatively long lived, are readily available and have high energies permitting lower doses [138–140]. Targeted radionuclide therapy involves their delivery to target cancer cells by means of specific carrier molecules. Several polyaminopolycarboxylic acids have been modified to conjugate Bi(III) radionuclides to proteins [20,136,141]. The complexes should be thermodynamically stable, but the main requirement is a high stability *in vivo*. Thus,

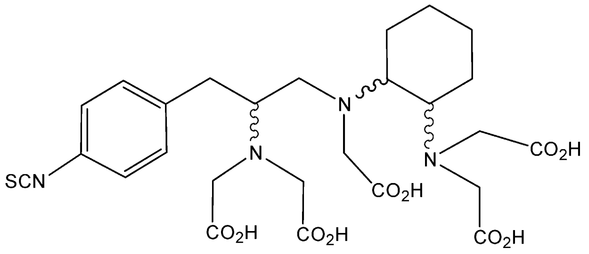


Chart 2. Functionalized dtpa derivatives for complexation of bismuth(III) radioisotopes evaluated *in vivo* [20]. The N atoms on the 1,2-cyclohexyl moiety are in *trans*-position giving rise to two pairs of enantiomers.

despite the high stability constant of the Bi(III)–dtpa complex, its bifunctional derivatives do not have an acceptable stability *in vivo*. In contrast, anions of macrocyclic polyaminopolycarboxylic acids, such as H_4dota or H_4teta form thermodynamically and kinetically stable complexes with Bi(III) [129], but the rate of complexation reactions is slow [142]. It is known that a solution to increasing the stability of the complexes is the preorganization of the ligands [143]. Thus, preorganization of

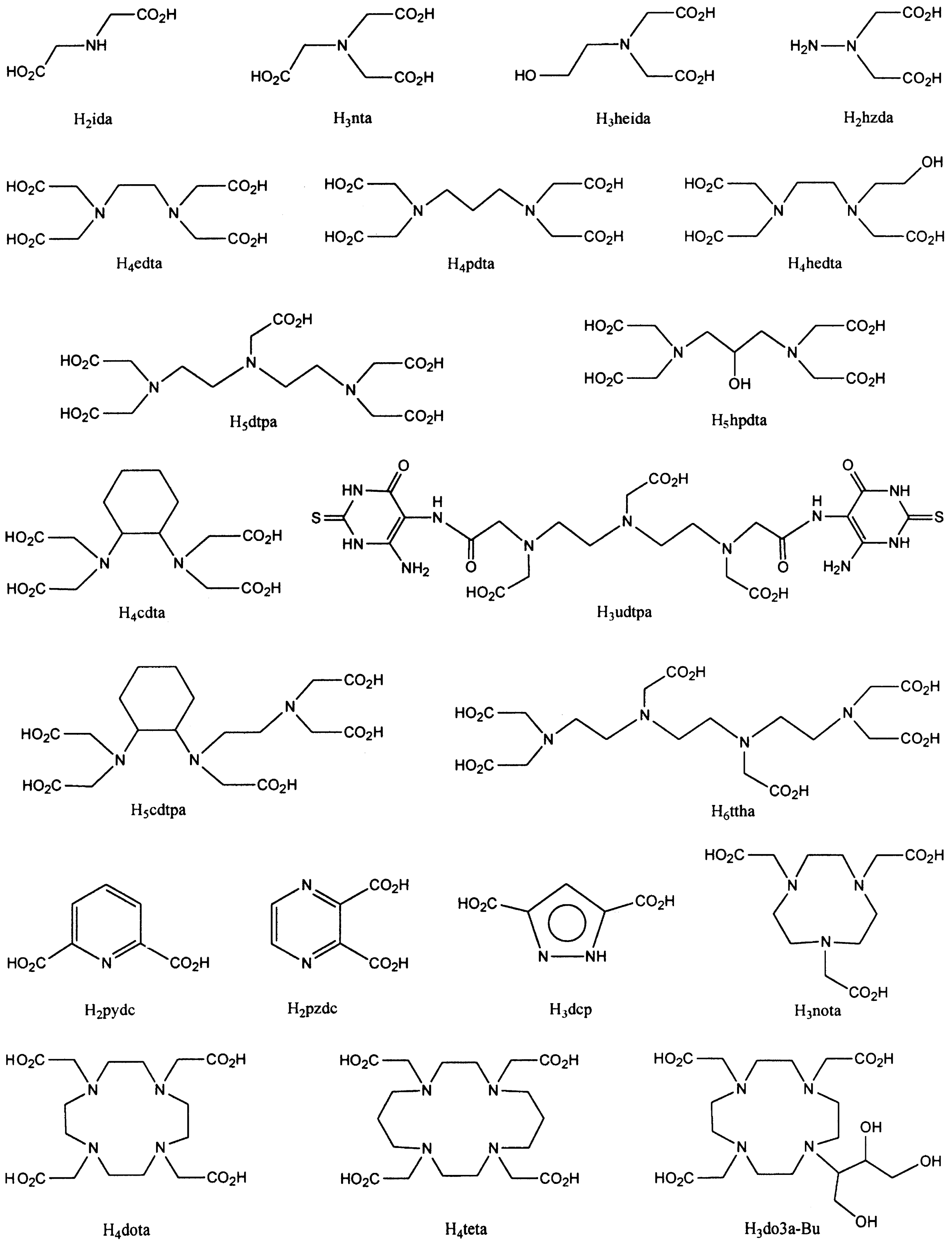


Chart 3. Aminopolycarboxylic and polyaminopolycarboxylic acids mentioned in this paper.

the dtpa and ttha ligands by introducing alkyl groups, aryl or a *trans*-cyclohexyl moiety allowed not only for an increase in the stability, but also maintained the rapid complex formation in solution [20,144]. For instance, CHX–dtpa ligands (Chart 2) permit a rapid complexation with $^{212/213}Bi$ and assure a high stability *in vivo* when conjugated to proteins [20].

Recently, the compound Cs[Bi(edta)]·H_2O has been proposed as a solute for the separation of lipoproteins as a density gradient in the ultracentrifugation [145]. It was shown that a useful density gradient is formed within a few hours, beginning with a homogeneous solution. The migration of lipoproteins is efficient, permitting their rapid separation. The properties that make this complex suitable for the separation of lipoproteins are its high solubility, small partial volume, low viscosity, and most importantly, Cs[Bi(edta)]·H_2O rapidly forms a gradient from a homogeneous solution.

Some bismuth(III) nitrilotriacetate complexes $M_3[Bi(nta)_2]\cdot nH_2O$ ($M^+ = Na^+, K^+, Rb^+, Cs^+, NH_4{}^+, CH_6N_3{}^+$), and a mixed-ligand bismuth(III) complex $K[Bi(edta)(tu)_2]$ were shown to suppress the growth of sea bacteria (Ulva fenestrata) efficiently; however, the mechanism of their action remains unknown [146].

As pointed out earlier, bismuth complexes with polyaminopolycarboxylate ligands have many applications in analytical chemistry for both direct and indirect titrations [15–17]. Solutions of Bi–edta were recently used to design ion-selective electrodes for the determination of Bi(III) [147–149].

Na_2H_2edta was used as a complexing agent for the preparation of bismuth particles by thermal processes [150,151] and electrodeposition [152,153]. Particles of various dimensions and morphology, from microparticles [152,153] to nanoplates [149] and nanorods [151], were obtained. The role of the complexing agent in these processes is believed to affect the redox potential of Bi^{3+} and influence the speed of Bi^{3+} release from the $Bi(edta)^-$ complex, thus controlling, to a certain extent, the reduction speed.

APC and PAPC acids have recently found extensive use as complexing agents in nanotechnology. For instance, H_3nta and H_4edta are used for the deposition of bismuth chalcogenide films and nanoparticles, namely Bi_2S_3 thin films [154,155], nanorods [156,157], nanoribbons [158], and nanofibers [159]; $CuBiS_2$ thin films [160]; Bi_2Se_3 nanocrystals [161], nanowires [162], nanospheres and nanorods [163]; Bi_2Te_3 thin films [164,165], nanorods [166], nanocapsules [167,168] and nanotubes [168]. These chalcogenide materials display a range of useful electric and thermoelectric properties with potential applications in nanoelectronic and energy conversion devices.

$[Bi(nta)(H_2O)_2]$ was shown to display piezoelectric properties [169]. A series of Co(III)–Bi(III) heterometallic complexes have been proposed as dielectric materials with high dielectric constants [170–173]. These materials might be further thermally processed to obtain semiconductors or ionic conductors.

APC and PAPC acids have been used for the preparation of bismuth-containing oxide materials by different chelate and sol–gel techniques. H_3nta, H_3heida and H_4edta have been used as chelate agents to produce a range of bismuth-containing superconducting oxides, among them Y–Bi–Cu–O [174], Bi–Pb–Sr–Ca–Cu–O [174–176], or Bi–Sr–Ca–Cu–O systems [177–179].

The complexing route was also used to produce piezoelectric Nb–Ta–Bi–O [180], ferroelectric Sr–Bi–Ta–O [181] and BIMEVOX [182] materials. Bismuth-substituted iron garnet films of $BiDy_2Fe_5O_{12}$ can be conveniently prepared by a so-called modified Pechini process, in which H_4edta rather than citric acid is used as a chelating agent [183–185].

Another significance of bismuth heterometallic complexes is their potential use as single-source precursors for Bi-containing mixed-metal materials [186,187]. Aminopolycarboxylic and polyaminopolycarboxylic acids are demonstrated to be particularly interesting candidates for the assembly of heterometallic complexes owing to numerous N and O coordination sites and flexible connection modes. The advantage of using heterometallic APC and PAPC complexes as precursors for mixed-oxide systems is the *a priori* imposed stoichiometry of the metal, the availability of the ligands and the fact that the synthesis can be performed even in aqueous solutions. A number of recently reported papers revealed the potential application of heterobimetallic Bi-containing polyaminocarboxylates as precursors for such ternary oxide-type materials. For instance, perovskite-type Cu_2BiO_4, sillenite-type $Bi_{26-x}Co_xO_{40-\delta}$, or $LnBiO_3$ can be prepared from corresponding precursors at low temperature [65,87,106,126,188]. The main advantage of starting from a molecular precursor is the control of stoichiometry at the molecular level. Devillers and co-workers [106,126,188] showed that heterobinuclear BiM(ttha) complexes, M = Y, La or Pr generate upon thermal decomposition in air the corresponding mixed oxides, $BiYO_3$, $BiLaO_3$ and $BiPrO_3$. Pyrolysis of $Cu[Bi(edta)_2]\cdot 9H_2O$ in air gives Bi_2CuO_4 at a relatively low temperature, 360 °C [65].

Bismuth(III) tris-aminocarboxylato complex with 2-quinolinecarboxylic acid $Bi(quic)_3$ acts as a catalyst for the oxidation of styrene oxide to benzoic acid in DMSO in the presence of O_2 [189]. Finally, a number of heterometallic Bi(III)–Co(III), Bi(III)–Cu(II), and Bi(III)–Ln(III) complexes based on nta and edta, as well as the products of their pyrolysis, proved to be efficient catalysts in radiolytic water decomposition [190–192].

7. Concluding remarks

Bi(III) is a borderline metal ion with a preferential interaction with ligands bearing soft donor groups [1,7,193,194]. Nevertheless, APC and PAPC ligands bearing both hard carboxylate groups and soft amine groups, form thermodynamically very stable complexes with this metal ion. Thus, despite the strong hydrolysis undergone by Bi(III) in aqueous media, multidentate APC and PAPC ligands efficiently stabilize it under physiological and even higher pH conditions. This allows the use of some of these ligands as carrier molecules for $^{212/213}Bi$ isotopes for radiotherapy [20,136,141,142]. In spite of the large interest shown in the coordination properties of these ligands and the attention paid in recent years to the possible involvement of Bi(III) complexes in anti-cancer radiotherapies, studies dealing with formation equilibria of Bi(III) PAC and PAPC complexes are still rare. A greater deal of research directed towards the formation equilibria of similar complexes with higher stability *in vivo* and lower cytotoxicity would be greatly desirable. The next step would probably be the optimization of the biocompatibility through the design of new ligands.

APC and PAPC ligands show a high affinity to Bi(III), usually exhibiting the maximum denticity. A range of different arrangements have been found, from monomeric to polymeric, the presence of bridging carboxylate groups being a common structural feature.

There is a great potential for bismuth(III) heterometallic APC and PAPC complexes as single-source molecular precursors in the preparation of mixed-oxide materials [65,87,106,126,188]. Their remarkable air and moisture stability makes these systems particularly attractive from the technological point of view. On the other hand, it would be of great interest to attempt to introduce other metals and to produce other stoichiometries in Bi(III) APC and PAPC heterometallic complexes. By virtue of their high versatility, some of them may find a place in developing new materials, especially with regard to nanoscale applications. By varying the stability and the structure of the precursors, one may expect to influence the quality of the final materials.

In conclusion, Bi(III) APC and PAPC complexes are essential for $^{212/213}$Bi use in nuclear medicine, but much is to be done to improve the biocompatibility and *in vivo* stability of the complexes. Heterometallic Bi(III) APC and PAPC complexes are promising precursors for a range of bulk oxide materials, however little work has been reported on their use in nanomaterial synthesis. Due to their high stability and diversity of the coordination architectures, the potential of Bi(III) APC and PAPC complexes is yet to be realized.

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Appendix A. Abbreviations

Aminopolycarboxylic and polyaminopolycarboxylic acids	
H_2ida	Iminodiacetic acid
H_3heida	β-Hydroxyethyliminodiacetic acid
H_3nta	Nitrilotriacetic acid
H_4edta	Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
H_5dtpa	Diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid
H_4hedta	*N*-2-Hydroxyethyl-ethylenediamine-*N*,*N*′,*N*′-triacetic acid
H_4cdta	1,2-Cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
H_5hpdta	2-Hydroxy-1,3-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
1,3-H_4pdta	1,3-Propylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
H_6ttha	Trietylenetetraamine-*N*,*N*,*N*′,*N*″,*N*‴, *N*‴-hexaacetic acid
H_3nota	1,4,7-Triazacyclononane-1,4,7-triacetic acid
H_4dota	1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid
H_3do3a–Bu	10-[2,3-Dihydroxy-(1-hydroxymethyl)propyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid
H_4teta	1,4,8,11-Tetraazacyclotetradecane-1,4,8,11-tetraacetic acid
H_4egta	Ethyleneglycol bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic acid
H_5cdtpa	1,2-Cyclohexanediaminedietylentriamine-*N*,*N*,*N*′,*N*″,*N*‴-pentaacetic acid
H_3udtpa	Diethylenetriamine-*N*,*N*′,*N*″-triacetate-*N*,*N*″-bis(4,5-diamino-6-hydroxy-2-mercaptopyrimidine)
H_2hzda	Hydrazine-*N*,*N*-diacetic acid
H_2pzdc	Pyrazine-2,3-dicarboxylic acid
H_3dcp	3,5-Pyrazoledicarboxylic acid
H_2pydc	Pyridine-2,6-dicarboxylic acid
Hquic	2-Quinolinecarboxylic acid
H_4dotmp	1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetramethylene phosphonic acid
Others	
M^{n+}	Metal cation
X^-	Monoanionic ligand
CN	Coordination number
tu	Thiourea
py	Pyridine
pyda	Pyridine-2,6-diamine
an	Aniline
o-, *m*-, *p*-tol	*ortho*-, *meta*-, *para*-Toluidine
H_2ssa	Salicylaldehyde semicarbazone
tsc	Thiosemicarbazide
ala	β-Alaninate-ion
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
Hdmg	Monodeprotonated 2,3-butanedione-dioxime
Hchdd	Monodeprotonated 1,2-cyclohexanedione-dioxime
ADE	Anisotropic displacement ellipsoid
BTP	Bicapped trigonal prism
TTP	Tricapped trigonal prism
SA	Square antiprism
MSA	Monocapped square antiprism
BSA	Bicapped square antiprism
D	Dodecahedron
IR	Infra-red
NMR	Nuclear magnetic resonance
MS	Mass spectrometry
ESI-MS	Electrospray ionization-mass spectrometry
TG	Thermogravimetry
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
HTXRD	High temperature X-ray diffraction

Note: All structures were re-created from the cif-files available from the Cambridge Structural Database using the SHELXTL software package (version 6.10, 2000) [195]. Aminopolycarboxylic and polyaminopolycarboxylic acids mentioned in this work are presented in Chart 3.

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