Syntheses and Structures of Bismuth(III) Complexes with Nitrilotriacetic Acid, Ethylenediaminetetraacetic Acid, and Diethylenetriaminepentaacetic Acid

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The reactions of bismuth subcarbonate with nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and diethylenetriaminepentaacetic acid (DTPA) were used to synthesize the respective bismuth complexes: (nitrilotriacetato)bismuth(III) dihydrate (**1**), (hydrogen ethylenediaminetetraacetato)bismuth(III) dihydrate (**2**), and bis(guanidinium) (diethylenetriaminepentaacetato)bismuthate(III) tetrahydrate (**3**). The structures of all three complexes were determined by single-crystal X-ray studies. In **1** the ligand is completely deprotonated, so that the resulting complex is neutral. The bismuth is eight-coordinate, the coordination sphere being completed by two water molecules and the O2 and O3′ oxygens from an adjacent Bi(NTA) molecule. The best description appears to be that of a bicapped trigonal prism. In the Bi(HEDTA) complex, **2**, the ligand is singly protonated to give 3– charge. The EDTA ligand coordinates in a hexadentate fashion involving the two nitrogen atoms and four of the carboxylate oxygen atoms of the EDTA ligand. The Bi atom is eight-coordinate in a bicapped trigonal prism arrangement. There are no coördinated water molecules. The Bi(DTPA) complex, **3**, was isolated as the guanidinium(1+) salt. In **3** the Bi atom is nine-coordinated with a monocapped square antiprism arrangement, using the three nitrogens and five oxygen atoms from the DTPA ligand and one O from an adjacent molecule. There are no coordinated water molecules. The Bi(DTPA) is the most soluble of the three complexes. Valence bond sums were calculated and are given for all three complexes. The antibacterial activities of the three complexes **1–3** were determined, and the least soluble complex, **1**, was found to be the most active. Crystallographic data: **1**, $C_6H_6NO_6Bi{\cdot}2H_2O$, monoclinic, $P2_1/n$, $a = 6.242(1)$ Å, $b = 20.927(3)$ Å, $c = 8.307(1)$ Å, $\beta = 102.49(1)°$, $Z = 4$; **2**, $C_{10}H_{13}N_2O_8Bi{\cdot}2H_2O$, monoclinic, Cc, $a = 17.196(2)$ Å, $b = 6.837(1)$ Å, $c = 13.277(2)$ Å, $\beta = 105.74(1)°$, $Z = 4$; **3**, $C_{16}H_{30}N_9O_{10}Bi{\cdot}4H_2O$, monoclinic, $P2_1/n$, $a = 15.113(3)$ Å, $b = 10.720(2)$ Å, $c = 17.091(3)$ Å, $\beta = 102.72(2)°$, $Z = 4$.

Introduction

Metallic bismuth has been known for about 500 years although the element was not identified as such until 1530.[1] Various bismuth salts have been used for medicinal purposes for at least 200 years, but the use of heavy-metal salts for human ailments has been discouraged.[2] However, the recent discovery that a colloidal bismuth subcitrate (CBS) was useful in treating peptic ulcers has increased the interest in bismuth compounds.[2–7] A further stimulus for bismuth chemistry has been the question of relativistic effects in the heavy elements[8] and the use of bismuth in high-temperature superconductors.[9]

Our interest in bismuth chemistry began with the preparation and characterization of bismuth complexes of the planar multidentate ligands DAPSC and PHENSC,[10–12] similar to those reported recently.[13] The complexes with DAPSC and PHENSC were surprisingly water soluble, which is not common for bismuth complexes. Therefore, we decided to focus our attention on the synthesis of water-soluble bismuth complexes with carboxylate-containing ligands. The ligands nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and diethylenetriaminepentaacetic acid (DTPA) are a series of carboxylate ligands that are good complexing agents for a variety of metal ions. The syntheses of Bi(HEDTA)[14] and (guanidinium)Bi(EDTA)[15] have been reported, but no structural data are available.[16] The bismuth complexes of NTA and DTPA have not been previously synthesized. We now wish to report the syntheses and single-crystal studies of the bismuth complexes with these three ligands. These complexes have also been tested for antibacterial activity. Details of the syntheses, crystal structures, and preliminary tests for antibacterial activity will be presented herein.

Experimental Section

Materials. Bismuth subcarbonate ($(BiO)_2CO_3$), NTA, EDTA, and DTPA were all commercial products and were used as supplied. The procedure used for all three complexes was similar to that reported for the synthesis of Bi(HEDTA).[14]

(Nitrilotriacetato)bismuth(III) Dihydrate (1). To a boiling solution of 0.107 g (0.561 mmol) of NTA in 60 mL of H_2O was added 0.142 g (0.279 mmol) of $(BiO)_2CO_3$. After 12 h of stirring, all solids had dissolved. The solution was filtered while hot, and the clear, colorless filtrate was

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0020-1669/94/1333-0088$04.50/0

Table 1. Crystallographic Data

	1	2	3
	A. Crystal Data (298 K)		
a, Å	6.242(1)	17.196(2)	15.113(3)
b, Å	20.927(3)	6.837(1)	10.720(2)
c, Å	8.307(1)	13.277(2)	17.091(3)
β, deg	102.49(1)	105.74(1)	102.72(2)
V, Å^3	1059.4(3)	1502.4(4)	2701.0(9)
d_{calc}, g cm^{-3}	2.716	2.358	1.942
empirical formula	$C_6H_6NO_6Bi{\cdot}2H_2O$	$C_{10}H_{13}N_2O_8Bi{\cdot}2H_2O$	$C_{16}H_{30}N_9O_{10}Bi{\cdot}4H_2O$
fw	433.13	534.24	789.53
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	Cc	$P2_1/n$
Z	4	4	4
F(000), electrons	800	1016	1568
crystal size, mm^3	0.30 × 0.26 × 0.20	0.39 × 0.22 × 0.16	0.65 × 0.54 × 0.07
	B. Data Collection (298 K)		
radiation/λ, Å	Mo Kα/0.710 73	Mo Kα/0.710 73	Mo Kα/0.710 73
mode	ω scan	ω scan	ω scan
scan range	symmetrically over $X°$ about K$\alpha_{1,2}$ maximum (X = 1.5, 1.2, and 1.2 for **1**–**3**, respectively)offset 1.0 and −1.0 in ω from K$\alpha_{1,2}$ maximum		
scan rate, deg min^{-1}	3–6	2–4	3–6
2θ range, deg	3–55	3–50	3–55
ranges of hkl	$0 \le h \le 8$	$0 \le h \le 20$	$0 \le h \le 18$
	$0 \le k \le 27$	$0 \le k \le 8$	$0 \le k \le 12$
	$-10 \le l \le 10$	$-15 \le l \le 15$	$-20 \le l \le 20$
no. of total reflns measd	2744	1495	5117
no. of unique reflns	2446	1367	4640
abs coeff μ(Mo Kα), mm^{-1}	16.67	11.77	6.61
min/max transm	0.035/0.105	0.070/0.200	0.331/0.669
	C. Structure Refinement		
S, goodness-of-fit	1.44	1.29	1.38
no. of reflns used, $I > 2\sigma(I)$	1943	1288	3631
no. of variables	149	206	423
R/R_w[a] %	3.47/4.09	2.24/2.72	3.79/4.09
R_{int}, %	3.54	0.00	2.03
max shift/esd	0.001	0.001	0.001
min peak in diff Fourier map, e Å^{-3}	−2.54	−1.49	−1.75
max peak in diff Fourier map, e Å^{-3}	2.29	1.52	1.34

[a] Relevant expressions are as follows, where in the footnote F_o and F_c represent respectively the observed and calculated structure factor amplitudes. Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$. $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$. $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

allowed to evaporate. The crystalline product was recrystallized once from H_2O, and crystals suitable for an X-ray analysis were obtained. Anal. Calc (found) for $C_6H_{10}NO_8Bi$: C, 16.64 (17.16); H, 2.33 (1.99); N, 3.23 (3.28).

(Hydrogen ethylenediaminetetraacetato)bismuth(III) Dihydrate (2). To 100 mL of H_2O was added 1.25 g (4.29 mmol) of EDTA. The solution was heated to boiling, and 1.20 g (2.36 mmol) of $(BiO)_2CO_3$ was added in small increments. After 30 min, the mixture was filtered while hot, and the clear, colorless filtrate was allowed to evaporate.

Colorless crystals suitable for an X-ray single-crystal analysis were formed. Anal. Calc (found) for $C_{10}H_{17}N_2O_{10}Bi$: C, 22.48 (22.16); H, 3.21 (3.15); N, 5.24 (5.19).

Bis(guanidinium) (Diethylenetriaminepentaacetato)bismuthate(III) Tetrahydrate (3). To a boiling solution of 50 mL of H_2O and 0.928 g (2.36 mmol) of DTPA was added 0.600 g (1.18 mmol) of $(BiO)_2CO_3$. After 1 h all solid was in solution. To the cooled solution was added 0.425 g (2.36 mmol) of guanidine carbonate ($(C(NH_2)_3)_2CO_3$). The reaction mixture was heated slowly to boiling, and after 2 h, the solution was filtered and the clear, colorless filtrate allowed to evaporate slowly. The resulting white solid was recrystallized three times from H_2O to obtain crystals suitable for an X-ray analysis. Anal. Calc (found) for $C_{16}H_{38}N_9O_{14}Bi$: C, 24.34 (24.90); H, 4.85 (4.61); N, 15.97 (16.53).

Antibacterial Studies. Crystals of Bi(NTA), Bi(HEDTA), and Bi(DTPA) were placed in sterile 100 mm diameter petri plates. Approximately 20 mL of melted plate-count agar (Difco) with 0.05 g/mL of 2,3,5-triphenyltetrazolium chloride (henceforth TTC) and approximately 10^5 colony-forming units (CFU) of *Escherichia coli*, C-3000 per mL, were added to the plates. After 24 h of incubation, the plates were red from the reduction of the TTC except for clear areas, where the bacterial growth had been inhibited. The diameters of the zones of inhibition were measured.[17] The areas of inhibition appeared to be the greatest for Bi(NTA) and Bi(HEDTA). Bi(DTPA) showed no apparent area of inhibition although the color in the dish appeared to be lighter than those in the other two. Bi(NTA) and Bi(HEDTA) were selected for further tests.

The use of antibacterial agents as coatings on bandages was simulated by soaking filter papers at room temperature and in heated solutions of the Bi(NTA) and Bi(HEDTA) complexes and allowing them to dry. The filter papers were then tested for antibacterial activity as described above. In all cases, antibacterial activity was observed, with the most prominent occurring in the heated solution of Bi(NTA). A study of the effect of temperature was carried out by making coated filter papers at three controlled temperatures. A saturated solution of Bi(NTA) at 30 °C was prepared by stirring an excess of the solid in 5 mL of H_2O in a beaker heated in an oil bath. Two filter papers were soaked in the solution and allowed to dry. A similar procedure was followed for 60 and 90 °C, care being taken to ensure that the solution was at equilibrium and saturated. These filter papers were then tested for antibacterial activity as described above. As expected, the filter papers coated at 90 °C showed greater areas of inhibition than those made at 60 and 30 °C.

X-ray Structural Studies. Single-crystal X-ray data for all three complexes were collected at room temperature on a Siemens P3m/V diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The cell parameters for **1**–**3** were determined using 40, 28, and 36 reflections, respectively, that were in the range $20.0° \le 2\theta \le 22.0°$. Four standard reflections were measured after every 96 reflections to monitor instrument and crystal stability. The maximum corrections of intensity based on the standard reflections were 1, 4, and 3%, respectively. Absorption corrections were applied by measuring the crystal faces. SHELXTL PLUS was used in the absorption and all subsequent calculations.[18] The linear absorption coefficients, scattering factors for

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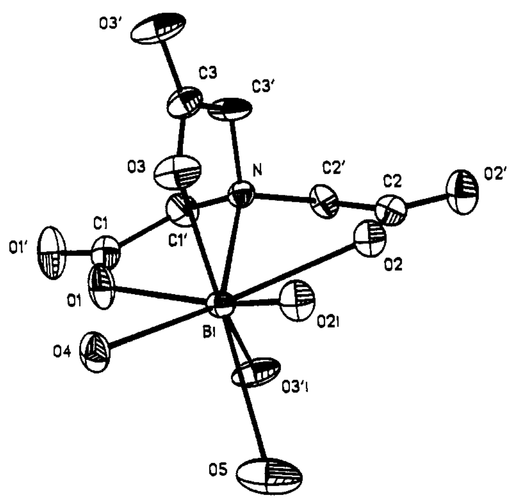

Figure 1. View of the Bi(NTA) complex showing the thermal ellipsoids and the atomic numbering. Atoms O2i and O3'i are from different molecules.

Table 2. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of Compound **1**

atom	*x*	*y*	*z*	*U*
Bi	0.08221(5)	0.094810(10)	0.43940(4)	0.01760(10)
N	0.0602(12)	0.1436(3)	0.7101(9)	0.020(2)
O1	0.0532(12)	0.2020(3)	0.4132(8)	0.033(3)
O1′	0.1090(13)	0.2974(3)	0.5236(9)	0.044(3)
O2	0.1018(11)	0.0164(3)	0.6692(8)	0.026(2)
O2′	0.2339(12)	–0.0001(3)	0.9368(8)	0.036(3)
O3	–0.2757(10)	0.1021(3)	0.4465(8)	0.030(2)
O3′	–0.5332(10)	0.1309(4)	0.5768(9)	0.039(2)
O4	–0.0856(12)	0.1154(3)	0.1556(8)	0.029(2)
O5	0.3527(12)	0.0308(5)	0.2697(10)	0.053(3)
C1	0.0976(14)	0.2392(4)	0.5353(12)	0.027(3)
C1′	0.131(2)	0.2104(4)	0.7093(12)	0.029(3)
C2	0.1781(13)	0.0355(4)	0.8161(11)	0.022(3)
C2′	0.2058(15)	0.1072(4)	0.8453(10)	0.023(3)
C3	–0.3390(14)	0.1232(4)	0.5702(12)	0.025(3)
C3′	–0.1708(14)	0.1382(6)	0.7274(12)	0.032(3)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathrm{A}_{ij}$ where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

all the atoms, and the anomalous-dispersion corrections were taken from the usual source.[19] The structures were solved by the heavy-atom method and Fourier syntheses. The refinement was done by full-matrix least-squares procedures using anisotropic thermal parameters. The H atoms were located in difference Fourier syntheses where possible in **1** and **2**, but the water H atoms in **3** could not be located in the difference maps. The H atoms in the cation of **3** together with those of C3 and C6 were placed in idealized positions with fixed thermal parameters. In the case of **2**, the space group is chiral so that the chirality parameter,[20] η, also was refined. The final value of 1.03 ± 0.06 indicates that the chirality as shown in Figure 1 and the parameters in Table 2 correspond to the correct enantiomer.

The final fractional coordinates of the non-hydrogen atoms are given in Tables 2–4. A selection of bond distances and angles involving the bismuth atoms is given in Table 5. The hydrogen atomic coordinates, distances and angles involving the hydrogen atoms, and a complete list of distances and angles in the ligands are available as supplementary material.

Results

The reaction of bismuth subcarbonate with NTA, EDTA, and DTPA is a convenient method for the synthesis of bismuth complexes of these acids. However, preliminary studies with weaker acids such as picolinic or dipicolinic acid suggest that a p*K* of about 5 may be too weak for a reaction with the bismuth subcarbonate. Our results also show that partially deprotonated as well as fully deprotonated complexes can be prepared with polyprotic acids such as EDTA and DTPA. This suggests that the solubility of bismuth complexes of EDTA and DTPA might be varied by changing the corresponding cation.

Table 3. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of Compound 2

atom	*x*	*y*	*z*	*U*
Bi	0.0	0.12068(4)	0.0	0.02009(11)
O1	0.1362(5)	0.1168(10)	0.0113(7)	0.033(3)
O1′	0.2626(5)	0.1691(14)	0.1119(8)	0.046(3)
O2	–0.1514(5)	0.0000(15)	–0.0637(9)	0.056(3)
O2′	–0.2776(5)	0.0472(14)	–0.0606(7)	0.040(3)
O3	–0.0415(5)	0.4449(14)	–0.0609(7)	0.033(3)
O3′	–0.0031(5)	0.7487(10)	–0.0641(6)	0.037(3)
O4	0.0338(5)	–0.0447(11)	0.1563(6)	0.033(3)
O4′	0.0119(7)	–0.1408(12)	0.3037(8)	0.049(4)
N1	0.0727(6)	0.3664(11)	0.1263(8)	0.025(3)
N2	–0.0930(5)	0.2209(12)	0.1141(7)	0.023(3)
C1	0.1544(6)	0.287(2)	0.1736(9)	0.031(3)
C1′	0.1892(7)	0.187(2)	0.0944(9)	0.032(4)
C2	–0.1779(6)	0.244(2)	0.0529(9)	0.033(4)
C2′	–0.2032(7)	0.082(2)	–0.0284(9)	0.031(4)
C3	0.0780(6)	0.549(2)	0.0652(9)	0.027(3)
C3′	0.0032(9)	0.5826(13)	–0.0234(6)	0.021(3)
C4	–0.0880(8)	0.061(2)	0.1936(9)	0.033(4)
C4′	–0.0092(8)	–0.0484(15)	0.2195(8)	0.031(4)
C5	0.0298(7)	0.4059(14)	0.2093(9)	0.027(3)
C6	–0.0602(7)	0.4077(14)	0.1667(9)	0.025(3)
O	0.1868(5)	0.2631(14)	–0.1826(8)	0.050(3)
O′	0.3003(6)	–0.011(2)	–0.1832(8)	0.059(4)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_2\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathrm{A}_{ij}$ where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

A thermal ellipsoid drawing of **1** given in Figure 1 shows that the NTA ligand is coordinating in a tetradentate fashion involving the nitrogen atom and three carboxylate oxygens. The ligand is completely deprotonated, so that the resulting complex is neutral. The bismuth is actually eight-coordinate, as shown in Figure 1, the coordination sphere being completed by two water molecules and the O2 and O3′ oxygens from an adjacent Bi(NTA) molecule, forming a "dimeric" subunit. The eight-coordinate Bi atom is surrounded by one N and seven oxygen atoms. The polyhedron was analyzed by calculating the angles between facial planes consisting of three atoms bonded to the central bismuth atom.[21] The best description appears to be that of a bicapped trigonal prism consisting of two triangular faces (O1, O3, O4 and O2, O5, O3′) and the square face (O1, O4, O3′, O5). The capping atoms are N and O2′. This is not the usual polyhedron for eight-coordination but can be viewed as the intermediate between the square antiprism and the dodecahedron, the two polyhedra usually considered for eight coordination.[22] However, the lack of two planes containing four atoms that are either perpendicular or parallel suggests that the description is a proper one.

A view of the Bi(HEDTA) complex, **2**, is shown in Figure 2. The EDTA ligand coordinates in a hexadentate fashion involving the two nitrogen atoms and four of the carboxylate oxygen atoms. There are no coordinated water molecules. The ligand is singly protonated to maintain a 3– charge, so that the formulation as HEDTA is correct. The proton has been assigned to O1 on the basis of bond lengths in the carboxylate groups. In carboxylates 2–4 the C–O bond distances are equivalent, indicating conjugation of the double bond after deprotonation. The C–O bond distances in carboxylate 1 are not equivalent. The Bi atom is eight-coordinate, two N's and six O's, also in a bicapped trigonal prism arrangement. In this case, the square face is O1, N1, O3, O4′,

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Table 4. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for the non-Hydrogen Atoms of Compound 3

atom	*x*	*y*	*z*	*U*
Bi	0.95368(2)	–0.59373(3)	0.64925(2)	0.02632(9)
O1	0.9342(4)	–0.6038(5)	0.4966(3)	0.039(2)
O1′	0.8917(4)	–0.4767(6)	0.3911(3)	0.047(2)
O2	0.8528(4)	–0.7657(5)	0.6306(3)	0.039(2)
O2′	0.7321(4)	–0.8683(6)	0.5647(4)	0.052(2)
O3	0.9271(4)	–0.3674(5)	0.6630(3)	0.035(2)
O3′	0.9018(4)	–0.2220(6)	0.7482(4)	0.053(2)
O4	1.0428(4)	–0.7867(5)	0.6395(3)	0.036(2)
O4′	1.0651(4)	–0.9856(5)	0.6739(3)	0.043(2)
O5	1.0667(4)	–0.4932(5)	0.7694(3)	0.040(2)
O5′	1.1834(4)	–0.5205(6)	0.8721(3)	0.053(2)
N1	0.7923(4)	–0.5411(6)	0.5598(4)	0.031(2)
N2	0.8432(4)	–0.5504(6)	0.7381(4)	0.034(2)
N3	1.0014(4)	–0.7269(6)	0.7808(4)	0.032(2)
C1	0.8103(6)	–0.4639(8)	0.4935(5)	0.036(3)
C1′	0.8846(5)	–0.5205(7)	0.4578(5)	0.035(3)
C2	0.7465(6)	–0.6589(8)	0.5276(5)	0.037(3)
C2′	0.7791(5)	–0.7723(8)	0.5775(5)	0.037(3)
C3	0.8717(6)	–0.4301(7)	0.7789(5)	0.038(3)
C3′	0.9017(6)	–0.3322(8)	0.7260(5)	0.036(3)
C4	0.9950(6)	–0.8584(7)	0.7577(5)	0.032(3)
C4′	1.0369(5)	–0.8801(7)	0.6845(5)	0.033(3)
C5	1.0966(7)	–0.6956(8)	0.8203(6)	0.039(3)
C5′	1.1165(5)	–0.5583(7)	0.8215(5)	0.034(3)
C6	0.7396(6)	–0.4761(8)	0.6104(5)	0.037(3)
C7	0.7489(6)	–0.5419(10)	0.6907(6)	0.044(3)
C8	0.8477(6)	–0.6560(9)	0.7965(5)	0.039(3)
C9	0.9429(6)	–0.6937(9)	0.8376(5)	0.041(3)
C10	0.8902(6)	–0.0948(8)	0.5375(5)	0.037(3)
N11	0.8505(5)	–0.0827(7)	0.5988(4)	0.046(3)
N12	0.9518(4)	–0.1811(6)	0.5374(4)	0.042(3)
N13	0.8675(5)	–0.0177(7)	0.4752(4)	0.047(3)
C20	1.1985(6)	–0.2021(8)	0.7879(5)	0.042(3)
N21	1.2283(5)	–0.0874(7)	0.7814(4)	0.048(3)
N22	1.2520(5)	–0.2842(7)	0.8336(5)	0.056(3)
N23	1.1175(5)	–0.2352(7)	0.7504(5)	0.055(2)
O11	1.1255(13)	–0.331(2)	0.9794(9)	0.239(12)
O12	0.9927(14)	–0.161(2)	0.9042(8)	0.29(2)
O13	0.5554(11)	–0.934(3)	0.5128(11)	0.38(2)
O14	1.023(2)	0.041(2)	0.9620(12)	0.142(13)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{A}_{ij}$ where $\mathbf{A}_{ij}$ is the dot product of the *i*th and *j*th direct space unit cell vectors.

with the triangular faces being O2, O3, O4′ and O4, N1, O1. Whether the bicapped trigonal prism is a consequence of the multidentate nature of the ligands or is related to the size of the Bi atom is difficult to decide at this time. We are looking at other distorted eight-coordinate complexes to determine the frequency of appearance of the bicapped trigonal prism.

Figure 3 is a view of the Bi(DTPA) complex, 3. The ligand is octadentate and is completely deprotonated giving a 5– charge, which is balanced by the Bi^{3+} and two guanidinium(1+) cations. The Bi atom is nine-coordinate, using three nitrogens and six carboxylate oxygens. There are no coordinated water molecules. The sixth carboxylate oxygen comes from another Bi(DTPA), yielding a "dimerlike" unit. It should be noted that the synthesis was attempted without the guanidinium cations but did not yield a crystalline product. Of the three bismuth carboxylate complexes, Bi(DTPA) is the most soluble, presumably due to the anionic nature of the complex ion. The coordination around the Bi is best described as a monocapped square antiprism. The square faces are N3, O4, O5, O1′ and N2, O1, O2, O3, with N1 being the capping atom.

Two features that appear to be common to complexes **1**–**3** together with the citrate complexes reported earlier[5–7] are the dimerlike nature of the complexes in the crystalline state and the irregularity of the Bi–donor atom distances. These features may be related to the requirement that the valence bond sum,[23] henceforth VBS, must be 3 and the question of the stereochemical activity of the lone pair on the Bi(III) ion.[24,25] The formation of a complex of any metal ion with a multidentate ligand represents a compromise between the steric interactions in the ligand and the steric and electronic requirements of the metal. The Bi(III) case is complicated since there is a lone pair on the metal ion which could be stereochemically active; in this case, the metal polyhedra should be one larger than the "observed polyhedra" on the basis of the locations of the donor atoms. In our cases, this would lead to tricapped trigonal prisms in the cases of **1** and **2** and a bicapped square antiprism for **3**, not unreasonable nor unusual polyhedra.

Table 5. Summary of the Bond Distances (Å) and Selected Bond Angles (deg) Surrounding the Bismuth Atoms[a]

Bond Distances

atoms	**1**	**2**	**3**
Bi–N1	2.500(8)	2.461(8)	2.639(6)
Bi–N2		2.577(9)	2.536(7)
Bi–N3			2.626(6)
Bi–O1	2.258(6)	2.306(9)	2.562(5)
Bi–O2	2.501(6)	2.642(9)	2.368(5)
Bi–O3	2.253(7)	2.400(9)	2.479(5)
Bi–O4	2.403(6)	2.295(7)	2.494(5)
Bi–O5	2.767(9)		2.599(5)
Bi–O1′i			2.686(6)
Bi–O2i	2.665(6)		
Bi–O3′i	2.435(6)	2.678(7)	
Bi-O4′i		2.673(11)	

Bond Angles

atoms	**1**	**2**	**3**
Ni–Bi–N2		72.5(3)	70.2(2)
N2–Bi–N3			71.3(2)
N1–Bi–O1	70.2(2)	69.2(3)	62.3(2)
N1–Bi–O2	65.4(2)		66.6(2)
N1–Bi–O3	72.6(2)	69.4(3)	
N2–Bi–O2		63.6(3)	
N2–Bi–O3			67.8(2)
N2–Bi–O4		69.2(3)	
N3–Bi–O4			63.6(2)
N3–Bi–O5			62.6(2)
VBS-BA	3.26	3.04	2.89
VBS-OB	3.52	3.31	3.04

[a] the VBS-BA was calculated using the VBS method with values from ref 23, and VBS-OB used the values from ref 26; see text for details.

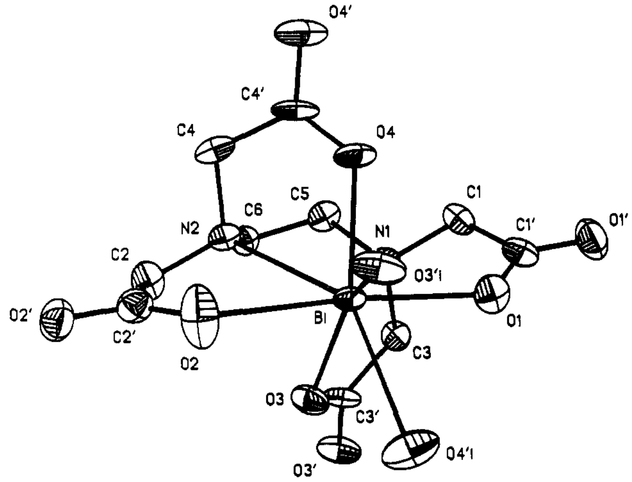

Figure 2. View of the Bi(HEDTA) complex showing the thermal ellipsoids and the atomic numbering. Atoms O3′i and O4′i are from a different molecule.

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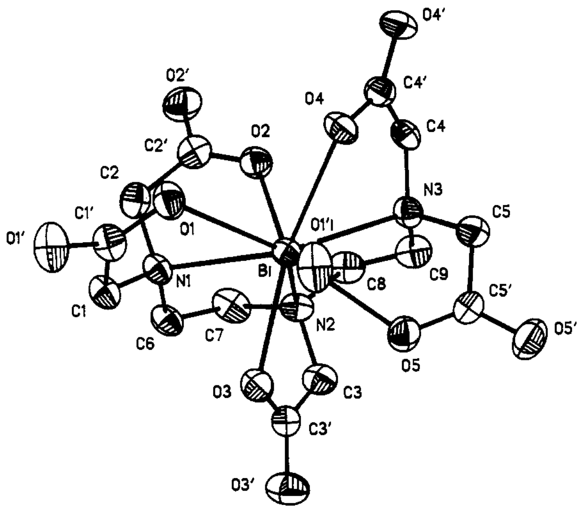

Figure 3. View of the Bi(DTPA) cation showing the thermal ellipsoids and the atomic numbering. Atom O1'i is from a different molecule.

The VBS has been proposed to equal the valence or charge on an atom or ion and is calculated by summing $\exp[(r_c - r_o)/B]$ for each bond to the atom or ion in question, where r_c is a constant for a particular bond type, r_o is the observed bond length, and B is a constant taken to be 0.37. The VBS for each complex was calculated and is given in Table 5. The r_c values used were 2.094 Å for Bi–O and 2.184 Å for Bi–N[23] for the case given as VBS-BA and 2.12 Å for Bi–O and 2.23 Å for Bi–N[26] for the case given as VBS-OB. The BA values are in better agreement than the OB values. Using the BA parameters, the corresponding values for the various citrate complexes[5,6] range from 2.86 to 3.23. We see that in all cases the BA values are close to the predicted value of 3.0, but some refinement of the Bi–O and Bi–N values is possible. We are continuing work along these lines. One reason for the VBS calculation was to establish the usefulness of the concept applied to bismuth. In addition, since the difference between a $Bi(H_2O)^{3+}$ and a BiO^{3+} cation is only two protons, which cannot always be located in an X-ray crystal structure determination, the VBS calculation might be useful in distinguishing between Bi(III) and Bi(V). The fact that the VBS calculation for the various Bi complexes gives 3.0 ± 0.2 suggests that the VBS may be a useful concept and may be applicable to coordination complexes. This view is supported by recent publications.[27]

The antibacterial activity of complexes **1**–**3** suggests that bismuth complexes might have a wider range of activity than was expected. The question of whether the complexes inhibited bacterial growth or were bactericidal remains to be determined. The fact that the least soluble complex, **1**, was the most active was unexpected. The reasons for this observation are being pursued.

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Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atomic coordinates, distances and angles involving the hydrogen atoms, and complete distances and angles in the ligands (13 pages). Ordering information is given on any current masthead page.

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