successfully stabilizes rare high-valent middle and later transition-metal centers of definitive oxidation states.

The structural properties of the polyamides produced in this study are relevant to current work on the ordering effects of hydrogen bonding. It is reasonable to assume that a combination of hydrogen-bond templates and restricted rotation about the C–N bonds contributes to the good yield of H_4[1] obtained under nondilute conditions. It is likely that manipulating solvent polarity to encourage hydrogen bond templates or to break up undesirable hydrogen bonds is an underutilized technique in the synthesis of amide-containing macrocycles.

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Registry No. A, 565-80-0; B, 17346-16-6; C, 73082-76-5; D·2HBr, 134389-70-1; E, 134389-66-5; F, 134389-67-6; G, 134389-69-8; G·2HBF$_4$, 136424-55-0; H[**2**]·2HBr, 136392-01-3; H_4[**1**]·CH_2Cl_2, 136392-02-4; H_4[**1**]·$C_2H_4Cl_2$, 136392-03-5; CuCl(η^3-**2**)·THF, 136392-05-7; diethylmalonyl dichloride, 54505-72-5; bromoisobutyryl bromide, 20769-85-1.

Supplementary Material Available: Listings of atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, bond lengths involving non-hydrogen atoms, bond angles involving non-hydrogen atoms, and close contacts involving hydrogen atoms and complete details of the crystal structure analysis for H_4[**1**]·$C_2H_4Cl_2$ and CuCl(η^3-**2**)·THF (32 pages); listings of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Spectroscopic Properties of Bismuth Citrate Compounds. 1. Crystal Structures of $K_{5-x}(NH_4)_x[Bi_2(cit)_2(Hcit)](H_2O)_y$ ($x = 0.25$, $y = 13$) and $(NH_4)_8[Bi_2(cit)_2(Hcit)_2(H_2O)_4](H_2O)_2$

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This paper describes the synthesis, characterization, and structure of five different products all containing Bi(III) and citrate. These compounds have the general formula $K_{5-x}(NH_4)_x[Bi_2(cit^{4-})_2(Hcit^{3-})](H_2O)_y$ (**1**, x = 0.25–1.0, y = 13), $K_{3-x}(NH_4)_x[Bi(cit^{4-})]_3(H_2O)_y$ (**2**, x = 0–0.5, y = 3–5), $K_{3-x}(NH_4)_x[Bi(cit^{4-})]_3(H_2O)_6$ (**3**, x = 1–2, y = 6), $K_{3-x}(NH_4)_x[(BiO)_2Bi(cit^{4-})_2](H_2O)_6$ (**4**, x = 2–3, y = 6), and $(NH_4)_4[Bi(cit^{4-})(Hcit^{3-})(H_2O)_2](H_2O)$ (**5**). Compounds **1** and **5** have been fully characterized by using three-dimensional X-ray analysis; compounds **2–4** have been characterized by elemental analysis and spectroscopy only. The compound $K_{4.75}(NH_4)_{0.25}[Bi_2(cit)_2(Hcit)](H_2O)_{13}$ (**1**) crystallizes in the space group $P\bar{1}$ with a = 11.801 (4) Å, b = 12.973 (3) Å, c = 15.856 (5) Å, α = 98.15 (2)°, β = 108.39 (2)°, γ = 100.91 (2)°, V = 2208.1 Å^3, and Z = 2. The asymmetric unit, which contains two Bi ions on a distance of 4.17 Å, is linked to another unit by an inversion center to form a tetranuclear subunit with additional Bi–Bi distances of 5.82 and 5.85 Å. These tetranuclear units are linked into a two-dimensional network with large meshes, which contain the potassium and ammonium ions and the lattice water molecules. The compound $(NH_4)_4[Bi(cit)(Hcit)(H_2O)_2](H_2O)$ (**5**) crystallizes in the space group $P2_1/c$ with a = 8.998 (2) Å, b = 9.492 (8) Å, c = 27.021 (6) Å, β = 99.42 (2)°, V = 2274.2 Å^3, and Z = 4. The asymmetric unit, which contains one Bi ion, is paired to itself into a dinuclear subunit with a Bi–Bi contact of 5.97 Å. In both compounds the bismuth ions are coordinated by nine oxygens of the citrate anions, with two of the citrate carboxylic groups being bidentately bonded to each bismuth ion, which in compound **5** two of the nine oxygens are water oxygens. One of the nine oxygens coordinated to each bismuth ion is an alcoholic oxygen. The distance to this alcoholic oxygen appears to be the shortest Bi–O contact (about 2.12 Å), the longest Bi–O distance being ca. 3.0 Å. The oxygen to oxygen (water and citrate) and nitrogen (ammonium) distances lie in a range that is characteristic for hydrogen bonding. Compounds **2** and **3** are obtained from solutions of different Bi/cit ratios. Whether type **2** or type **3** is formed is determined by the amount of ammonia in the solutions, but the several batches of type **2** (and also of type **3**) are structurally the same (on the basis of IR, X-ray powder). Compound **4** can be obtained from bismuth citrate solutions containing an equimolar ratio or small excess of H_4cit. The solution behavior of the crystalline compounds obtained has been investigated by using ^1H and ^{13}C NMR spectroscopy. All compounds, except for type **4**, show a similar behavior. At low pH (<7), rapid ligand exchange is observed and all citrates are averaged on the NMR time scale. At high pH the citrates are hardly coordinated to Bi(III). However, under high-concentration conditions (high solubility is attained only under basic conditions), coordinated citrates can be detected besides uncoordinated ones. In the case of compound **4**, coordinated citrates are detected even in the low-pH regions. These coordinated citrates become averaged (rapid exchange) by adding free citrate and by raising the pH.

Introduction

Bismuth is the least toxic metal of the As, Sb, Bi triad, which is unusual, since toxicity normally increases down a group in the periodic table. In fact, bismuth and its salts were once widely used in the treatment of syphilis and yaws. Furthermore, bismuth compounds have been used in medicine for two hundred years in a variety of gastrointestinal disorders, also because of their demulcent properties.[2]

Among the modern, bismuth-based ethical pharmaceuticals, DE-NOL (trademark of Gist-brocades N.V.), having colloidal bismuth subcitrate (CBS) as active ingredient, is probably the most interesting. This compound, which is a complex bismuth salt of citric acid (H_4cit), is a very effective peptic ulcer healing agent, and its pharmacological properties were thoroughly investigated from the viewpoint of pharmacology in the last two decades.[3]

The use of CBS in peptic ulcer patients also resulted in significantly lower relapse rates when compared with other ulcer-healing agents.[3] These lower relapse rates are now known to be

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(2) (a) Reynolds, J. E. F., Ed. *Martindale, The Extra Pharmacopoeia*, 20th ed.; The Pharmaceutical Press: London, 1982. (b) Manhart, M. D. *Rev. Infect. Dis.* **1990**, *12*, S11–S15.

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due to bactericidal action of CBS against *Helicobacter pylori* (formerly called *Campylobacter pylori*) both in vitro and in vivo[4] and the subsequent beneficial effect on *H. pylori* related gastritis.[3e,5]

In spite of much pharmacological and clinical information on CBS, its chemical information is strictly limited. According to the most recent Merck index[3j] bismuth subcitrate sol (dried)—this is abbreviated as CBS—can be described by the approximate formula $K_3(NH_4)_2Bi_6O_3(OH)_5(Hcit)_4$. The compound is a polynuclear complex bismuth citrate salt, coprecipitated with potassium or ammonium citrate.

CBS is often referred to as $K_3Bi(Hcit)_2$ (H_4cit being citric acid; Hcit being the triple-dehydronated, trianionic, form). However, a mixture of potassium hydroxide, bismuth citrate, and citric acid in the 3:1:1 ratio, corresponding to 3 K^+, Bi^{3+}, and 2 $Hcit^{3-}$, is not soluble in water, while CBS is very soluble.

Various crystalline species have been found on the ulcer craters of patients treated with CBS, depending upon the pH;[7] thus, at pH 1.5 only amorphous, weakly refractile material is seen, while at pH 2 complex crystalline structures resembling wheat sheaves or mulberries are formed. At pH 3, distinct diamond shapes appear, and at pH's 4 and 5, rhomboids and needles develop. Both bismuth oxychloride (BiOCl) and bismuth citrate are known to be constituents of the precipitates.[8] In fact one may predict certain species for the bismuth citrate complexes by considering the ratio of bismuth, citric acid, and, if any, potassium or ammonium as countercations, using the fact that citric acid has at least four coordinating or chelating oxygen donors, i.e. three carboxylic groups and one hydroxy group. Therefore, our interest has been focused on the composition and structure of the main species present in CBS. During this investigation, several crystalline bismuth citrate complexes were prepared by varying parameters, such as pH and the $Bi/H_4cit/KOH/NH_4OH$ ratios, during the synthesis.

In this paper, we report the syntheses of five different bismuth citrate complexes, their spectroscopic characterization, and two crystal structures of them, which were determined by three-dimensional X-ray analysis. Furthermore, the solution behavior of these compounds has been studied by ^1H and ^{13}C NMR spectroscopy. A subsequent paper[9] will deal with the comparison between CBS and compounds **1**–**5** in the solid state and in aqueous solutions.

Experimental Section

Materials. Citric acid monohydrate ($H_4cit{\cdot}H_2O$, Brocacef bv), bismuth citrate (BiHcit, ICN), potassium hydroxide (85%, Merck), ammonia solution (25%, Merck), deuterium oxide (99.8%, Aldrich), 10% NaOD in D_2O (Aldrich), and 10% DCl in D_2O (Aldrich) were commercially obtained and used without further purification.

Preparation. $K_{4.75}(NH_4)_{0.25}[Bi_2(cit)_2(Hcit)](H_2O)_{14}$ (1). A 10-mL volume of ammonia solution was added dropwise to 20 mL of suspended aqueous solution containing bismuth citrate (10 g, 0.025 mol) and citric acid monohydrate (2.66 g, 0.013 mol) to give a clear solution. A 10-mL volume of aqueous solution containing potassium hydroxide (4.15 g, 0.063 mol) was slowly added to the solution while it was stirred. The mixture was concentrated to about one-third of the volume in a rotary evaporator. The solution was filtered and allowed to stand at 4 °C. After 1 week, white needles that separated were collected and washed with mixtures of water and methanol (3:1, 1:1, 1:3), methanol, and diethyl ether and dried in air. Yield: 3.8 g. Anal. Calcd for $C_{18}H_{40}N_{0.25}O_{34}K_{4.75}Bi_2$: C, 15.36; H, 2.86; N, 0.25; K, 13.19; Bi, 29.29. Found: C, 15.40; H, 2.86; N, 0.28; K, 12.5; Bi, 29.2. The present crystalline compound very easily looses lattice water in air, to become a powder. A single crystal suitable for X-ray crystallography was obtained in a similar way and mounted into a capillary with a small amount of solvent (water:methanol = 1:9).

$K_{3-x}(NH_4)_x[Bi(cit)]_3(H_2O)_y$ (2a). When **1** was recrystallized from hot water, a fine powdery product was obtained. The white product was collected and washed with mixtures of water and methanol (3:1, 1:1, 1:3), methanol, and diethyl ether and dried in air. Yield: 60–70%. Anal. Calcd for the formula $K_{2.7}(NH_4)_{0.3}[Bi(cit)]_3(H_2O)_4$: C, 15.76; H, 1.60; N, 0.31; K, 7.78; Bi, 45.6. Found: C, 15.94; H, 1.48; N, 0.30; K, 8.20; Bi, 45.4.

$K[Bi(cit)](H_2O)_y$ (2b). To 20 mL of suspended aqueous solution containing bismuth citrate (5 g, 0.013 mol) and citric acid monohydrate (2.66 g, 0.013 mol) was added 10 mL of aqueous solution containing potassium hydroxide (2.50 g, 0.038 mol). The suspended reaction mixture was stirred with heating for 2 days and then allowed to stand at room temperature. After a few days, a white precipitate obtained was collected, washed, and air-dried. Yield: 4.8 g. Anal. Calcd for KBi(cit)(H_2O), $C_{18}H_{20}O_{25}K_3Bi_3$: K, 8.49; Bi, 45.41; C, 15.66; H, 1.46. Found: C, 15.91; H, 1.43; K, 8.58; Bi, 45.6.

$K_{1.4}(NH_4)_{1.6}[Bi_3(cit)_3](H_2O)_6$ (3a). To 20 mL of suspended aqueous solution containing bismuth citrate (10 g, 0.025 mol) and citric acid monohydrate (2.66 g, 0.013 mol) was added an ammonia solution until the mixture became a clear solution. A 10-mL volume of an aqueous solution containing potassium hydroxide (0.828 g, 0.013 mol) was added to the solution. After filtration, the filtrate was concentrated to about half-volume under reduced pressure. The solution was allowed to stand at 4 °C for 2 months. The columnar crystals separated and were collected, washed with a mixture of water and methanol (3:1, 1:1, 1:3), methanol, and diethyl ether, and dried in air. Yield: 1.2 g. Anal. Calcd for $C_{18}H_{30.4}N_{1.6}O_{27}K_{1.4}Bi_3$: NH_3, 2.09; H_2O, 7.82; K, 3.96. Found: NH_3, 2.08; H_2O, 7.82; K, 3.7. This product gives the same infrared spectrum and the same X-ray diffraction pattern as those of a related product[9] with a different K/NH_4 ratio. Hence, the chemical formula was determined on the basis of the contents of K, NH_3, and H_2O.

$(NH_4)_3[(BiO)_2Bi(cit)_2](H_2O)_6$ (4a). Procedure 1. To a mixture of bismuth citrate (10 g, 0.025 mol) and citric acid monohydrate (2.66 g, 0.013 mol) in 30 mL of water was added 10 mL of ammonia solution. The solution was placed in a round-bottomed flask, which was connected with another round-bottomed flask filled with methanol and allowed to stand under reduced pressure. As methanol vapor diffused into the reaction mixture, a white finely divided powder started to separate. The powder was removed by filtration, and methanol vapor was diffused into the filtrate in the same way. After several days, cubic crystals that separated were collected, washed with mixtures of water and methanol (3:1, 1:1, 1:3), methanol, and diethyl ether, and dried in air. Yield: 3.2 g. Anal. Calcd for $C_{12}H_{32}N_3O_{22}Bi_3$: C, 12.04; H, 2.69; N, 3.51; O, 29.40; Bi, 52.36. Found: C, 12.38; H, 2.46; N, 3.61; O, 26.8; Bi, 52.7.

Procedure 2, Leading to a Slightly Different Product, $(NH_4)_3$-$[(BiO)_2Bi(cit)_2](H_2O)_3$. A 10-mL volume of ammonia solution was added to a suspended aqueous solution (30 mL) containing 10 g of bismuth citrate (0.025 mol). The solution was filtered and then concentrated to half of its volume in a rotary evaporator. From the solution cubic crystals started to separate in a few days. After 2 weeks, the crystals were collected, washed, and dried in air. Yield: 4.0 g. Anal. Calcd for $C_{12}H_{26}N_3O_{19}Bi_3$: C, 12.61; N, 3.68; H, 2.29; Bi, 54.84. Found: C, 12.60; N, 3.60; H, 2.31; Bi, 54.0.

$K_{1.4}(NH_4)_{1.6}[(BiO)_2Bi(cit)_2](H_2O)_5$ (4b). When **2a** was recrystallized from an ammonia solution, cubic crystals were formed. The compound shows the same crystal shape, the same infrared spectrum, and the same X-ray diffraction pattern as found for compound **4a**. Yield: less than 10%. The chemical formula was determined on the basis of the contents of K, NH_3, and H_2O. Anal. Calcd for $C_{12}H_{24.4}N_{1.6}O_{21}K_{1.4}Bi_3$: K, 4.52; NH_3, 2.25; H_2O, 7.45. Found: K, 4.3; NH_3, 2.30; H_2O, 7.7.

$(NH_4)_4[Bi(cit)(Hcit)(H_2O)_2](H_2O)$ (5). Into the filtrate from which **4a** was separated methanol vapor was further diffused. Needlelike crystals started to form, besides cubic crystals (**4a**). After crystallization, the mixture of the needles and cubes was separated manually, and then the pure needles were obtained. Yield: 4.2 g. Anal. Calcd for $C_{12}H_{31}N_4O_{17}Bi$: C, 20.23; H, 4.39; N, 7.86; O, 38.18; Bi, 29.34. Found: C, 20.31; H, 4.43; N, 7.94; O, 39.1; Bi, 28.9. The crystals were stable in air. An isolated long needle was cut to a suitable size for X-ray crystallography.

Instruments, Analyses, and Measurements. Carbon, hydrogen, nitrogen, oxygen, potassium, and bismuth analyses were carried out at Mikroanalytisches Labor Pascher, Bonn, Germany.

Water and ammonia contents were analyzed at the Analytical R&D Laboratories of Gist-brocades, Delft, The Netherlands.

Infrared spectra were recorded on a Perkin-Elmer Model 580 spectrophotometer using KBr disks.

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X-ray powder diffraction patterns were registered with a Nonius Guinier–de Wolff camera, using Cu Kα radiation.

All pH measurements were performed at 298 K. The pH meter was calibrated with Fisher certified solutions of pH 4.00 and 7.00.

^{1}H NMR spectra were recorded with a Bruker WM 300 spectrometer. D_2O was used as a solvent. Chemical shifts (δ) are reported in ppm relative to TMA (tetramethylammonium nitrate). The pH dependence of the chemical shifts of methylene protons of citrate was monitored by adding a trace amount of DCl and NaOD in D_2O (0.1 and 1 M). The pH values reported as pH* have not been corrected for deuterium isotope effects. ^{1}H NMR spectra of solutions with different citrate/bismuth ratios were measured at pH* 5.0. The solutions were prepared by adding stock citric acid monohydrate solution (10 mM) to a solution of bismuth citrate (10 mM). The stock solution of bismuth citrate was prepared by adding a trace amount of NaOD to suspended bismuth citrate in D_2O. As NaOD was added, bismuth citrate gradually started to dissolve, to yield a clear solution. ^{13}C NMR spectra were measured with a Bruker MSL-400 spectrometer and with a 10-mm tunable probe. Millipore water was used as a solvent. Chemical shifts are reported in ppm relative to DSS (sodium 4,4-dimethyl-4-silapentanesulfonate), which was dissolved in a 10% D_2O/H_2O mixture as a external standard. HCl and ammonia solutions were used to adjust the pH for monitoring the pH dependence of the spectra.

X-ray Methods and Structure Determination. In Table I the crystallographic data for the compounds $K_{4.75}(NH_4)_{0.25}[Bi_2(cit)_2(Hcit)](H_2O)_{13}$ (**1**) and $(NH_4)_4[Bi(cit)(Hcit)(H_2O)_2](H_2O)$ (**5**) are listed. Crystals of these compounds were mounted in a glass capillary and subjected to graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) on a four-circle Enraf-Nonius CAD4 diffractometer, operated in the ω/θ mode. The cell dimensions were determined from the setting angles of 24 reflections with $10° < \theta < 12°$. The scanning rate was adjusted to the required precision of $\sigma(I)/I = 0.01$ with a maximum scan time of 60 s per reflection. The instrument and crystal stability were checked every 5400 s of radiation time by measuring three reference reflections. Intensities were corrected for Lorentz and polarization effects. Absorption correction was applied by an empirical method.[10] Locally developed computer programs were used for the crystallographic calculations. The structures were solved by standard heavy-atom methods: The positions of the bismuth atoms were determined from a Patterson map. The positions of most of the other non-hydrogen atoms were obtained by using the program AUTOFOUR.[11] The atomic scattering factors were taken from ref 12. The citrate carbon bonded hydrogen atoms were placed at 0.95 Å from their parent atom. The H atoms of the ammonium ions and of the water molecules could not be located. No effort was made to calculate their positions. The oxygen atoms of the water molecules of compound **1** are strongly disordered. Not all of these water oxygens could therefore be located from difference Fourier maps, and some had to be given partial occupancy factors to match the electron density maps. Also, ammonium cations of compound **1** could not be located in difference Fourier maps. Most probably this cation is randomly present on the potassium positions and would then only account for at most 5% of the scattering power on these positions. Together with the strong disorder of the water oxygens, this accounts for the discrepancy between the chemical formula of compound **1** and the formula used in the refinement (see Table I). With the exception of the oxygen atoms of the water molecules of compound **1**, the non-hydrogen atoms were refined anisotropically.

The function minimized was $\sum w|F_o - F_c|^2$ with $w = 1/\sigma^2(F)$. The positions of the H atoms were coupled to their respective parent atom during refinement. The H atoms were assigned overall isotropic temperature factors yielding final B values of 3.98 Å^2 (**1**) and 2.04 Å^2 (**5**), respectively. Estimated standard deviations were calculated with the use of a correlation matrix.

The fractional coordinates of the non-hydrogen atoms are listed in Tables II and III. A selection of the atomic distances and bond angles is given in Tables IV and V. Lists of the atomic coordinates of the hydrogen atoms, of the non-hydrogen anisotropic thermal parameters, of the remaining bond distances and bond angles, and of the observed and calculated structure factors are available as supplementary material.[13]

Results and Discussion

Description of the Structure of $K_{4.75}(NH_4)_{0.25}[Bi_2(cit)_2(Hcit)](H_2O)$ (1). The asymmetric unit contains two bismuth atoms, three citrates, five potassium atoms (partially substituted by ammonium), and lattice water. The ammonium ions could not be located in the Fourier maps (see above). The atomic coordinates for the non-hydrogen atoms are given in Table II. The atomic numbering scheme for the citrates is given in Figure 1. In Table IV the relevant bond distances and angles are listed. The bismuth ions are coordinated by nine oxygen atoms of the three dehydronated citrates, whereby in both cases two of the carboxylic groups are bonded in a didentate manner. Two of the citrates are tetraionized (cit^{4-}); the third citrate is triionized (Hcit^{3-}). The alcoholic oxygen of two of the three citrates is involved in the bismuth coordination. These bismuth oxygen bonds are in fact the shortest Bi–O contacts (Bi1–O131 = 2.125 Å; Bi2–O231 = 2.120 Å) in the coordination sphere of both bismuth ions. There are no water molecules coordinated to the bismuth ions. The Bi ions in the dinuclear $[Bi_2(cit)_2(Hcit)]$ unit (see PLUTO[14] drawing

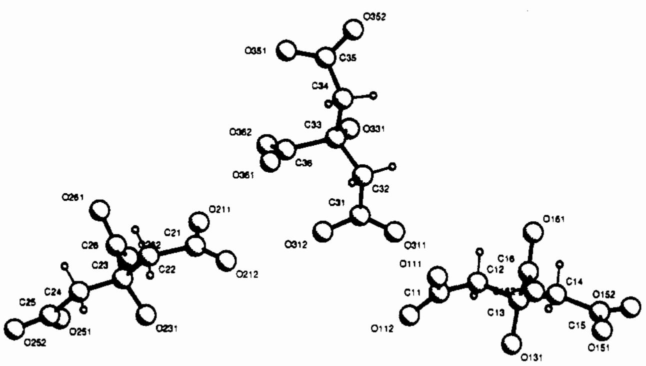

Figure 1. PLUTO[14] projection of the three crystallographic independent citrates of compound **1** with the atomic numbering scheme for the non-hydrogen atoms. The numbering system of citrates 1 and 2 also holds for the description of compound **5**.

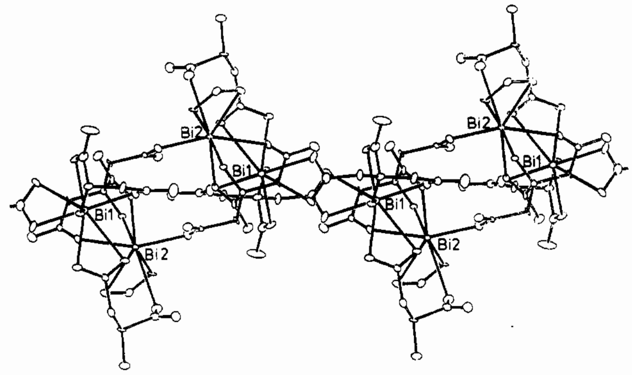

Figure 2. PLUTO[14] projection, showing the coordination of Bi1 and Bi2 in compound **1**.

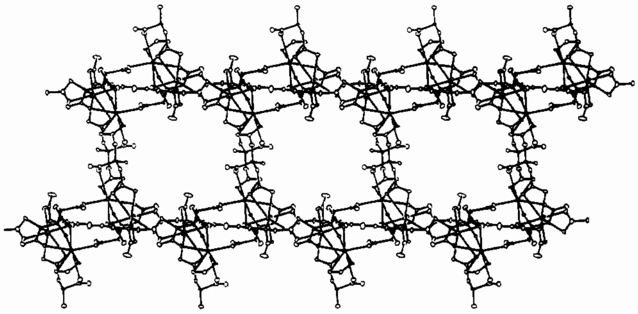

Figure 3. The bismuth–citrate network of compound **1**, showing the relatively large meshes, which contain the counterions and the lattice water molecules.

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Table I. Crystallographic Data for the Compounds $K_{4.75}(NH_4)_{0.25}[Bi_2(cit)_2(Hcit)](H_2O)_{13}$ (**1**) and $(NH_4)_4[Bi(cit)(Hcit)(H_2O)_2](H_2O)$ (**5**)

compd	**1**	**5**
formula based on anal. data	$C_{18}H_{40}Bi_2K_{4.75}N_{.25}O_{34}$	$C_{12}H_{31}BiN_4O_{17}$
fw	1407.66	712.37
D_x, g/cm³	2.04	2.07
a, Å	11.801 (4)	8.998 (2)
b, Å	12.973 (3)	9.492 (8)
c, Å	15.856 (5)	27.021 (6)
α, deg	98.15 (2)	90
β, deg	108.39 (2)	99.42 (2)
γ, deg	100.91 (2)	90
V, Å³	2208.1	2274.2
T, K	293	293
formula used in refinement[a]	$C_{18}H_{12}Bi_2K_5O_{33.25}$	$C_{12}H_8BiN_4O_{17}$
F(000)	1294	1308
crystallogr system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
Z	2	4
μ, cm⁻¹	84.3	77.7
cryst dimens, mm³	0.40 × 0.20 × 0.14	0.30 × 0.12 × 0.04
color, habit	white, needle	white, needle
hkl ranges	−19/19; 0/20; 25/25	−14/14; 0/15; 0/43
scan range θ, deg	2–35	2–35
transm factors	0.71–1.17	0.56–1.24
decay scatt power, %	26.6	18.1
no. of measd reflcns	20015	10670
no. of unique reflcns	19327	10495
no. used in refinement[b]	7683	4822
no. of params	492	308
R_f[c]	0.040	0.042
R_w[d]	0.052	0.047
agreement factor	1.11	1.53
max, min Δρ excursions, e/Å³	1.17, −2.08	0.96, −1.79

[a] See text. [b] $I > 2\sigma(I)$. [c] $R_f = \sum(||F_o| - |F||)/\sum|F_o|$. [d] $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w|F_o|^2]^{1/2}$.

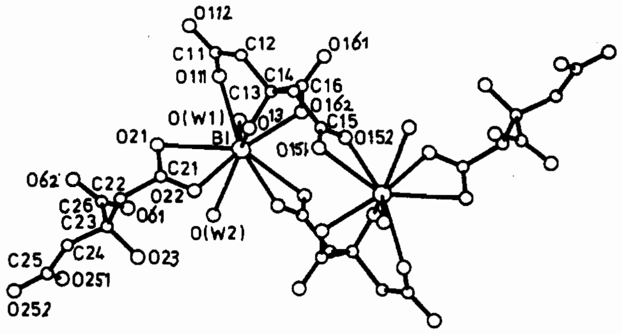


Figure 4. PLUTO[14] projection, showing the coordination of the dinuclear subunit of compound **5**.

in Figure 2) are at a distance of 4.17 Å. This unit is paired to itself by an inversion center to form a tetranuclear subunit with further Bi–Bi distances of 5.82 and 5.85 Å. The tetranuclear units are linked into a two-dimensional network (see Figure 3). This sheet has large meshes, which contain the (disordered) water molecules and the potassium (and ammonium) ions. The potassium ions are in contact with both citrate oxygens and water oxygens, with distances larger than 2.60 Å (see Table IV). The O–O distances below 3.3 Å are listed in Table IV. From these data it is clear that the citrates and the water molecules are interlinked by hydrogen bonds. A few apparently short (i.e. below 2.5 Å) distances indicate disorder between these oxygen positions.

Description of the Structure of $(NH_4)_4[Bi(cit)(Hcit)(H_2O)_2](H_2O)$ (5). The asymmetric unit contains one Bi^{3+} ion, one tetraionized citrate (cit^{4-}), one triionized ($Hcit^{3-}$) citrate, two coordinated water molecules, four ammonium ions, and one lattice water molecule. The atomic coordinates for the non-hydrogen atoms are given in Table III. The atomic numbering scheme for the citrates is given in Figure 1. In Table V the relevant bond distances and angles are listed. The $[Bi(cit)(Hcit)(H_2O)_2]$ unit is paired to itself by an inversion center into a dinuclear subunit (see Figure 4). These units are held together by van der Waals contacts and hydrogen bonds. The intramolecular Bi–Bi contact amounts to 5.97 Å. The bismuth ion is coordinated by

Table II. Atomic Coordinates (Bi × 10⁵, O46–O59 × 10³, Others × 10⁴) and Equivalent Isotropic Thermal Parameters (Bi, Å² × 10³; K, Å² × 10²; Others, Å² × 10) of the Non-Hydrogen Atoms of $K_{4.75}(NH_4)_{0.25}[Bi_2(cit)_2(Hcit)](H_2O)_{13}$ (**1**)

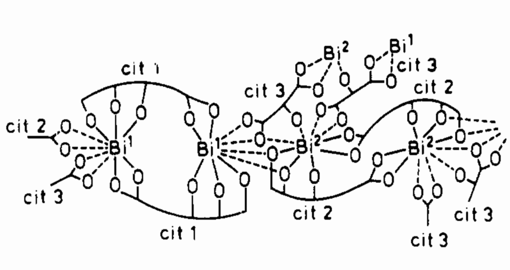
atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]
Bi1	36085 (3)	45993 (3)	30491 (2)	2069 (9)
Bi2	5684 (3)	31268 (3)	6916 (2)	2001 (9)
K3	−2736 (3)	3557 (2)	−840 (2)	375 (6)
K4	586 (3)	−1489 (2)	1852 (2)	519 (8)
K5	−1896 (3)	8372 (2)	−3290 (3)	521 (9)
K6	4226 (3)	7008 (2)	5498 (2)	573 (9)
K7	4334 (3)	3731 (2)	357 (2)	400 (7)
C11	2895 (8)	4363 (8)	4633 (6)	30 (2)
C12	2567 (8)	4040 (8)	5417 (6)	27 (2)
C13	3729 (8)	4178 (8)	6243 (6)	23 (2)
C14	3366 (8)	4001 (8)	7068 (6)	31 (2)
C15	4416 (9)	4161 (9)	7963 (7)	35 (3)
C16	4387 (9)	3315 (8)	6038 (7)	32 (3)
O111	3522 (7)	3863 (5)	4314 (4)	31 (2)
O112	2519 (7)	5112 (6)	4313 (4)	38 (2)
O131	4458 (5)	5236 (5)	6409 (4)	24 (2)
O151	5502 (7)	4453 (6)	7991 (4)	38 (2)
O152	4155 (7)	3995 (7)	8631 (5)	48 (2)
O161	3836 (8)	2363 (6)	5843 (7)	60 (3)
O162	5525 (7)	3622 (5)	6136 (5)	34 (2)
C21	1242 (9)	4131 (7)	−719 (6)	26 (2)
C22	1184 (8)	4541 (7)	−1588 (6)	24 (2)
C23	358 (8)	5338 (7)	−1751 (6)	23 (2)
C24	426 (9)	5801 (8)	−2558 (6)	27 (2)
C25	−301 (9)	6631 (7)	−2793 (6)	27 (2)
C26	−989 (8)	4714 (7)	−1955 (6)	22 (2)
O211	204 (7)	3671 (5)	−677 (4)	31 (2)
O212	2235 (7)	4272 (6)	−104 (4)	38 (2)
O231	793 (5)	6161 (5)	−958 (4)	24 (2)
O251	−1044 (6)	6798 (5)	−2393 (4)	29 (2)
O252	−214 (7)	7080 (5)	−3425 (5)	38 (2)
O261	−1473 (7)	3921 (5)	−2575 (4)	37 (2)
O262	−1545 (6)	5091 (5)	−1456 (4)	26 (2)
C31	3579 (8)	2464 (7)	2011 (6)	26 (2)
C32	3724 (8)	1385 (7)	1625 (6)	29 (2)
C33	2524 (8)	664 (7)	896 (6)	27 (2)
C34	2787 (9)	−429 (7)	589 (6)	29 (2)
C35	1628 (9)	−1276 (7)	29 (6)	29 (2)
C36	2113 (9)	1195 (7)	44 (6)	28 (2)
O311	3882 (7)	2747 (5)	2857 (4)	34 (2)
O312	3174 (7)	3062 (5)	1476 (4)	35 (2)
O331	1596 (6)	540 (5)	1276 (4)	30 (2)
O351	1004 (7)	−1238 (5)	−748 (5)	40 (2)
O352	1315 (6)	−2041 (5)	396 (4)	28 (2)
O361	2890 (7)	1429 (5)	−321 (4)	35 (2)
O362	1044 (7)	1304 (5)	−194 (4)	33 (2)
O41	405 (8)	9714 (7)	−2252 (6)	52 (1)
O42	709 (10)	6078 (8)	5391 (7)	73 (2)
O43	1985 (8)	2270 (7)	8159 (6)	53 (1)
O44	3237 (12)	7856 (11)	2603 (9)	96 (3)
O45	1426 (13)	7119 (12)	4185 (9)	105 (3)
O46	413 (2)	757 (1)	993 (1)	139 (5)
O47	304 (2)	814 (1)	826 (1)	146 (5)
O48	312 (2)	689 (2)	675 (1)	150 (5)
O49	387 (2)	653 (2)	789 (2)	78 (5)
O50	401 (2)	1032 (2)	876 (2)	79 (5)
O51	452 (3)	106 (2)	467 (2)	102 (7)
O52	135 (2)	94 (2)	476 (2)	80 (5)
O53	143 (2)	885 (2)	−369 (2)	93 (6)
O54	27 (3)	156 (2)	633 (2)	120 (8)
O55	279 (3)	969 (3)	341 (2)	57 (8)
O56	188 (4)	112 (4)	654 (3)	84 (11)
O57	293 (5)	878 (4)	517 (3)	92 (13)
O58	579 (6)	883 (5)	266 (4)	12 (1)
O59	330 (3)	712 (3)	929 (2)	45 (6)

[a] $B_{eq} = {}^{8}/_{3}\pi^2(\text{trace U})$.

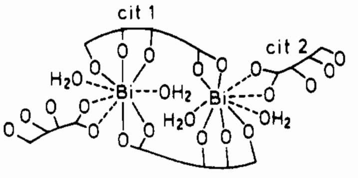
Table III. Atomic Coordinates (Bi × 10^5, Others × 10^4) and Equivalent Isotropic Thermal Parameters (Bi, $Å^2$ × 10^3; Others, $Å^2$ × 10) of the Non-Hydrogen Atoms of $(NH_4)_4[Bi(cit)(Hcit)(H_2O)_2](H_2O)$ (**5**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}[a]
Bi1	42817 (3)	33764 (3)	40442 (1)	1462 (4)
C11	2221 (8)	482 (7)	4314 (3)	17 (2)
C12	2675 (8)	771 (7)	4859 (3)	19 (2)
C13	3360 (8)	2243 (7)	4991 (3)	16 (2)
C14	3808 (8)	2329 (7)	5559 (3)	19 (2)
C15	4670 (9)	3675 (7)	5741 (3)	18 (2)
C16	2134 (8)	3362 (8)	4811 (3)	20 (2)
O111	2355 (7)	1424 (5)	3994 (2)	25 (1)
O112	1719 (7)	−715 (6)	4178 (2)	29 (2)
O131	4661 (4)	2432 (5)	4771 (2)	17 (1)
O151	4082 (6)	4847 (5)	5574 (2)	20 (1)
O152	5885 (7)	3614 (6)	6040 (3)	32 (2)
O161	949 (6)	3360 (6)	4989 (2)	28 (1)
O162	2393 (6)	4213 (5)	4474 (2)	19 (1)
C21	6670 (8)	1503 (8)	3801 (3)	21 (2)
C22	8050 (8)	816 (8)	3641 (3)	19 (2)
C23	8393 (8)	1430 (7)	3136 (3)	16 (2)
C24	9724 (8)	599 (8)	3007 (3)	18 (2)
C25	10217 (9)	1006 (9)	2513 (4)	24 (2)
C26	7015 (9)	1294 (8)	2715 (3)	20 (2)
O211	5382 (7)	1065 (6)	3611 (3)	35 (2)
O212	6862 (6)	2487 (6)	4116 (2)	21 (1)
O231	8794 (6)	2879 (5)	3223 (2)	21 (1)
O251	11392 (7)	335 (6)	2415 (3)	33 (2)
O252	9502 (8)	1874 (7)	2229 (3)	40 (2)
O261	6675 (7)	93 (7)	2559 (3)	37 (2)
O262	6335 (6)	2418 (6)	2575 (2)	26 (1)
O41	1964 (8)	3735 (8)	3232 (3)	59 (3)
O42	5658 (7)	4572 (6)	3230 (2)	29 (2)
O43	441 (7)	2365 (6)	1350 (2)	29 (2)
N31	7794 (8)	2036 (7)	193 (3)	25 (2)
N32	3330 (8)	2314 (8)	2141 (4)	41 (2)
N33	6819 (8)	3945 (8)	1712 (3)	31 (2)
N34	8978 (7)	4769 (7)	4082 (3)	27 (2)

[a] $B_{eq} = {}^8/_3\pi^2(\text{trace } U)$.



Comp. 1 (dimer → chain → sheet)



Comp. 5 (dimer)

Figure 5. Schematic comparison of the structural units of compound **1** and **5**.

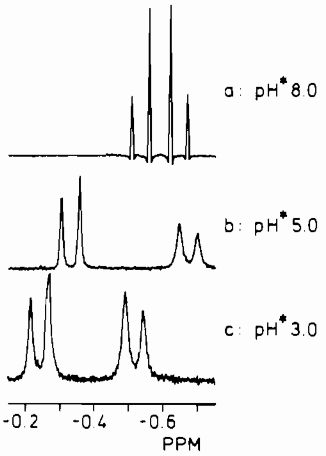


Figure 6. ^1H NMR spectra of compound **1** in D_2O (15 mM citrate) at different pH* values.

nine oxygen atoms, of which two belong to water molecules and the other seven belong to the two dehydronated citrates, whereby two of the carboxylic groups are bonded in a didentate manner. The alcoholic oxygen of one of the citrates is involved in the bismuth coordination. This bismuth oxygen bond is in fact the shortest Bi–O contact (Bi1–O131 = 2.136 Å) in the coordination sphere of the bismuth ion. The ammonium ions are in contact with both citrate oxygens and water oxygens, with distances larger than 2.70 Å (see Table V). The O–O distances below 3.3 Å are listed in Table V. From these data it is clear that the citrates, the ammonium ions, and the water molecules are involved in a hydrogen-bonding network.

Comparison of Structures of 1 and 5. All bismuth atoms in both **1** and **5** have more or less the same coordination geometry, with coordination number 9. Bi–O distances vary widely, i.e. from 2.12 to 3.04 Å for Bi(1) and Bi(2) in **1** and from 2.14 to 2.93 Å for Bi in **5**, but are significantly shorter than the sum of the van der Waals radii (3.47 Å). Structural data on Bi(III) compounds with oxygen ligands remain scarce,[15,16] but most mixed bismuth(III) oxides have only five or six neighbors at distances from 2.1 to 2.7 Å[16] and a small number of additional neighbors. Both structures (**1** and **5**) are compared on a schematic drawing in Figure 5. It is noteworthy that a unit Bi(cit) with tridentate citrate coordination is present in both structures **1** and **5**. In compound **5**, two of such dinuclear units are linked to each other through bridging by didentate carboxylates, giving units $Bi_2(cit)_2$, resulting in five donor atoms originating from this citrate. The coordination number of 9 is completed by two oxygen atoms from a didentate carboxylate of triionized citrate anion (citrate (2)) and two water molecules. When this dinuclear structure is considered as the most stable unit, compound **1** can be regarded as an aggregation of such units through citrate bridges. Thus, two coordinated water molecules in compound **5** are substituted by a didentate carboxylate from citrate(2), and the triionized citrate(2) corresponds to the triionized citrate(3) in compound **1**. The latter triionized citrates further connect two stable dinuclear units (citrate(1))Bi(1)Bi(1)(citrate(1)) and (citrate(2))Bi(2)Bi(2)(citrate(2)). Moreover, citrate(3) links the chains consisting of the two dinuclear units, resulting in a lattice with large cavities in which the water molecules and the counterions are located. Consequently, the dinuclear unit in **5** may be taken as the "subunit" in **1**. In fact, Bi–Bi and Bi–O distances in **5** are very close to the corresponding distances of (citrate(1))Bi(1)Bi(1)(citrate(1)) and (citrate(2))-Bi(2)Bi(2)citrate(2)) in **1**.

Comparison with Other Metal Citrate Complexes. During recent years quite a few other metal citrate structures have been described in detail in the solid state.[17,18] Very recently a renewed interest appears to have risen, and interesting trinuclear and tetranuclear species have been reported for aluminum citrate[18a] and a molybdenum oxo citrate,[18b] respectively.

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Table IV. Important Coordination Bond Lengths and Bi–Bi Contacts (Å) and Bond Angles (deg) of the Non-Hydrogen Atoms of $K_{4.75}(NH_4)_{0.25}[Bi_2(cit)_2(Hcit)](H_2O)_{13}$ (**1**)

Bi1–Bi2	4.1732 (4)	Bi2–O352^{l}	2.368 (5)	K4–O55^{c}	2.93 (3)	K6–O162^{q}	2.727 (9)
Bi2–Bi2^{n}	5.8193 (7)	Bi2–O351^{l}	2.811 (7)	K4–O362^{l}	2.798 (7)	K6–O311^{q}	2.776 (7)
Bi1–Bi1^{q}	5.8486 (6)	Bi2–O231^{n}	2.120 (7)	K4–O43^{m}	3.01 (1)	K6–O51^{q}	2.75 (3)
Bi1–O111	2.363 (7)	Bi2–O251^{n}	2.559 (7)	K4–O41^{n}	2.85 (1)	K6–O131	2.894 (7)
Bi1–O112	2.772 (7)	Bi2–O262^{n}	2.336 (5)	K4–O211^{l}	2.960 (7)	K6–O57	3.01 (2)
Bi1–O311	2.474 (7)	K3–O262	2.693 (7)	K5–O251	2.810 (8)	K6–O111^{q}	3.025 (7)
Bi1–O312	2.802 (7)	K3–O151^{a}	2.865 (8)	K5–O41	2.773 (8)	K7–O212	2.613 (9)
Bi1–O251^{n}	2.988 (6)	K3–O352^{l}	2.841 (7)	K5–O311^{n}	2.841 (9)	K7–O312	2.702 (9)
Bi1–O131^{q}	2.125 (6)	K3–O212^{n}	2.852 (7)	K5–O331^{n}	3.183 (8)	K7–O361	2.998 (7)
Bi1–O151^{q}	2.552 (8)	K3–O44^{n}	2.94 (1)	K5–O52^{n}	2.82 (3)	K7–O152^{e}	2.752 (9)
Bi1–O162^{q}	2.339 (6)	K3–O46^{o}	2.84 (2)	K5–O55^{p}	2.91 (4)	K7–O152^{q}	3.053 (8)
Bi1–O262^{n}	3.042 (6)	K3–O59^{o}	2.95 (2)	K5–O252	2.867 (7)	K7–O46^{q}	2.79 (2)
Bi2–O211	2.313 (7)	K3–O231^{n}	2.963 (7)	K5–O111^{n}	3.053 (7)	K7–O49^{q}	3.03 (2)
Bi2–O212	2.943 (7)	K4–O331	3.060 (8)	K6–O112	2.840 (7)	K7–O59^{q}	3.11 (2)
Bi2–O312	2.954 (8)	K4–O352	2.757 (8)	K6–O48	2.71 (2)	K7–O151^{q}	3.195 (7)
Bi2–O362	2.817 (8)						

O111–Bi1–O311	69.0 (3)	O211–Bi2–O212	47.9 (3)	O212^{n}–K3–O46^{o}	101.7 (4)	O212–K7–O312	73.0 (3)
O111–Bi1–O251^{n}	76.7 (2)	O312–Bi2–O362	68.1 (2)	O44^{n}–K3–O46^{o}	107.4 (4)	O212–K7–O361	87.8 (2)
O111–Bi1–O131^{q}	86.1 (3)	O312–Bi2–O352^{l}	139.4 (2)	O331–K4–O352	70.1 (2)	O212–K7–O152^{e}	81.4 (3)
O111–Bi1–O151^{q}	160.0 (2)	O312–Bi2–O231^{n}	142.9 (2)	O331–K4–O55^{c}	74.9 (8)	O212–K7–O152^{q}	94.0 (2)
O111–Bi1–O162^{q}	96.0 (3)	O312–Bi2–O251^{n}	73.0 (2)	O331–K4–O362^{l}	68.8 (2)	O212–K7–O46^{q}	152.0 (3)
O111–Bi1–O112	49.5 (3)	O312–Bi2–O262^{n}	77.4 (2)	O331–K4–O43^{m}	126.9 (3)	O212–K7–O49^{q}	135.1 (6)
O111–Bi1–O312	114.1 (3)	O362–Bi2–O352^{l}	71.5 (2)	O331–K4–O41^{n}	65.4 (3)	O312–K7–O361	67.7 (2)
O111–Bi1–O262^{n}	130.1 (3)	O362–Bi2–O231^{n}	146.1 (2)	O352–K4–O55^{c}	107.8 (9)	O312–K7–O152^{e}	147.9 (2)
O311–Bi1–O251^{n}	75.8 (2)	O362–Bi2–O251^{n}	112.6 (2)	O352–K4–O362^{l}	66.6 (2)	O312–K7–O152^{q}	103.6 (2)
O311–Bi1–O131^{q}	74.3 (2)	O362–Bi2–O262^{n}	140.7 (2)	O352–K4–O43^{m}	124.0 (2)	O312–K7–O46^{q}	112.0 (5)
O311–Bi1–O151^{q}	108.0 (3)	O362–Bi2–O212	82.7 (3)	O352–K4–O41^{n}	128.1 (3)	O312–K7–O49^{q}	68.2 (5)
O311–Bi1–O162^{q}	145.7 (2)	O352–Bi2–O231^{n}	75.7 (2)	O55^{c}–K4–O362^{l}	143.0 (8)	O361–K7–O152^{e}	92.6 (2)
O311–Bi1–O112	114.7 (3)	O352–Bi2–O251^{n}	120.6 (2)	O55^{c}–K4–O43^{m}	127.7 (9)	O361–K7–O152^{q}	170.2 (2)
O311–Bi1–O312	49.1 (3)	O352–Bi2–O262^{n}	141.7 (2)	O55^{c}–K4–O41^{n}	85.3 (8)	O361–K7–O46^{q}	70.2 (4)
O311–Bi1–O262^{n}	113.0 (3)	O231^{n}–Bi2–O251^{n}	77.3 (2)	O362–K4–O43^{m}	72.7 (3)	O361–K7–O49^{q}	97.4 (4)
O251^{n}–Bi1–O131^{q}	149.3 (2)	O231^{n}–Bi2–O262^{n}	72.8 (2)	O362–K4–O41^{n}	73.4 (2)	O152^{e}–K7–O152^{q}	97.1 (2)
O251^{n}–Bi1–O151^{q}	122.5 (2)	O251^{n}–Bi2–O262^{n}	72.7 (2)	O43^{m}–K4–O41^{n}	69.5 (3)	O152^{e}–K7–O46^{q}	82.4 (5)
O251^{n}–Bi1–O162^{q}	132.4 (2)	O231^{n}–Bi2–O351^{l}	82.7 (3)	O251–K5–O41	85.4 (2)	O152^{e}–K7–O49^{q}	142.2 (6)
O251^{n}–Bi1–O262^{n}	57.6 (3)	O231^{n}–Bi2–O212	119.1 (3)	O251–K5–O311^{n}	73.4 (2)	O152^{q}–K7–O46^{q}	110.6 (4)
O131^{q}–Bi1–O151^{q}	74.3 (2)	O262^{n}–Bi2–O351^{l}	143.5 (3)	O251–K5–O331^{n}	81.3 (2)	O152^{q}–K7–O49^{q}	74.5 (4)
O131^{q}–Bi1–O162^{q}	74.0 (2)	O262^{n}–Bi2–O212	65.5 (3)	O251–K5–O52^{n}	127.4 (6)	O46^{q}–K7–O49^{q}	67.2 (6)
O151^{q}–Bi1–O162^{q}	75.4 (3)	O352^{l}–Bi2–O351^{l}	48.9 (3)	O251–K5–O55^{p}	154.2 (8)	K3^{k}–O151–Bi1^{q}	111.5 (3)
O131^{q}–Bi1–O112	115.6 (3)	O352^{l}–Bi2–O212	114.1 (3)	O41–K5–O311^{n}	133.7 (3)	K7–O152–K7^{q}	82.9 (2)
O131^{q}–Bi1–O312	95.8 (3)	O251^{n}–Bi2–O351^{l}	75.9 (3)	O41–K5–O331^{n}	64.5 (3)	Bi1^{q}–O162–K6^{q}	120.0 (3)
O131^{q}–Bi1–O262^{n}	143.7 (3)	O251^{n}–Bi2–O212	125.3 (3)	O41–K5–O52^{n}	83.9 (5)	Bi1^{q}–O162–O44^{q}	106.9 (3)
O162^{q}–Bi1–O112	68.8 (3)	O351^{l}–Bi2–O362	69.6 (3)	O41–K5–O55^{p}	87.0 (6)	K7–O212–K3^{n}	106.4 (2)
O162^{q}–Bi1–O312	147.8 (3)	O351^{l}–Bi2–O212	150.8 (3)	O311^{n}–K5–O331^{n}	71.7 (2)	K5–O251–Bi1^{n}	90.7 (2)
O162^{q}–Bi1–O262^{n}	100.4 (3)	O351^{l}–Bi2–O312	110.6 (3)	O311^{n}–K5–O52^{n}	141.3 (4)	K5–O251–Bi2^{n}	124.3 (3)
O151^{q}–Bi1–O112	137.3 (3)	O212–Bi2–O312	64.9 (3)	O311^{n}–K5–O55^{p}	94.6 (8)	Bi1^{n}–O251–Bi2^{n}	97.3 (2)
O151^{q}–Bi1–O312	72.4 (3)	O262–K3–O151^{a}	70.8 (2)	O331^{n}–K5–O52^{n}	136.4 (5)	K3–O262–Bi2^{n}	127.0 (3)
O151^{q}–Bi1–O262^{n}	69.7 (3)	O262–K3–O352^{l}	110.0 (2)	O331^{n}–K5–O55^{p}	73.2 (8)	Bi1–O311–K5^{n}	101.7 (3)
O112–Bi1–O312	140.2 (3)	O262–K3–O212^{n}	63.0 (2)	O52^{n}–K5–O55^{p}	76 (1)	Bi1–O311–K6^{q}	98.4 (2)
O112–Bi1–O251^{n}	71.4 (3)	O262–K3–O44^{n}	86.0 (3)	O112–K6–O48	91.9 (4)	K5^{n}–O311–K6^{q}	98.8 (3)
O112–Bi1–O262^{n}	94.2 (3)	O262–K3–O46^{o}	164.3 (4)	O112–K6–O162^{q}	63.0 (2)	Bi2–O312–K7	107.9 (2)
O312–Bi1–O251^{n}	69.3 (3)	O151^{a}–K3–O352^{l}	155.6 (2)	O112–K6–O311^{q}	129.8 (2)	K4–O331–K5^{n}	81.9 (2)
O312–Bi1–O262^{n}	69.6 (3)	O151^{a}–K3–O212^{n}	75.3 (2)	O112–K6–O51^{q}	137.1 (6)	K4–O352–Bi2^{l}	100.7 (3)
O211–Bi2–O312	110.3 (2)	O151^{a}–K3–O44^{n}	79.8 (3)	O48–K6–O162^{q}	154.8 (4)	K4–O352–K3^{l}	106.6 (2)
O211–Bi2–O362	85.8 (2)	O151^{a}–K3–O46^{o}	102.7 (4)	O48–K6–O311^{q}	74.5 (4)	Bi2–O352–K3^{l}	102.8 (2)
O211–Bi2–O352^{l}	70.1 (2)	O352^{l}–K3–O212^{n}	127.7 (2)	O48–K6–O51^{q}	121.9 (8)	Bi2–O362–K4^{l}	89.5 (2)
O211–Bi2–O231^{n}	91.0 (3)	O352^{l}–K3–O44^{n}	76.0 (3)	O162^{q}–K6–O311^{q}	122.2 (3)	K5–O41–K4^{n}	93.2 (3)
O211–Bi2–O251^{n}	160.6 (2)	O352^{l}–K3–O46^{o}	82.0 (4)	O162^{q}–K6–O51^{q}	80.1 (6)	K3^{o}–O46–K7^{q}	104.7 (6)
O211–Bi2–O262^{n}	89.1 (2)	O212^{n}–K3–O44^{n}	145.1 (3)	O311^{q}–K6–O51^{q}	87.6 (5)	K4^{h}–O55–K5^{p}	89 (1)
O211–Bi2–O351^{l}	118.5 (3)						

[a] −1.0 + *x*, 0.0 + *y*, −1.0 + *z*. [b] 0.0 + *x*, −1.0 + *y*, −1.0 + *z*. [c] 0.0 + *x*, −1.0 + *y*, 0.0 + *z*. [d] 0.0 + *x*, −1.0 + *y*, 1.0 + *z*. [e] 0.0 + *x*, 0.0 + *y*, −1.0 + *z*. [f] 0.0 + *x*, 0.0 + *y*, 1.0 + *z*. [g] 0.0 + *x*, 1.0 + *y*, −1.0 + *z*. [h] 0.0 + *x*, 1.0 + *y*, 0.0 + *z*. [i] 0.0 + *x*, 1.0 + *y*, 1.0 + *z*. [k] 1.0 + *x*, 0.0 + *y*, 1.0 + *z*. [l] 0.0 − *x*, 0.0 − *y*, 0.0 − *z*. [m] 0.0 − *x*, 0.0 − *y*, 1.0 − *z*. [n] 0.0 − *x*, 1.0 − *y*, 0.0 − *z*. [o] 0.0 − *x*, 1.0 − *y*, 1.0 − *z*. [p] 0.0 − *x*, 2.0 − *y*, 0.0 − *z*. [q] 1.0 − *x*, 1.0 − *y*, 1.0 − *z*. [r] 1.0 − *x*, 2.0 − *y*, 1.0 − *z*. [s] 1.0 − *x*, 2.0 − *y*, 2.0 − *z*.

In the case of aluminum(III) citrate, all three citrates are tetraionized, i.e. cit^{4-}, one of which functions as a tridentate chelate ligand to the Al(III), just as we found for the compounds **1** and **5**. Interestingly, two independent triionized citrates (Hcit^{3-}) in $K_4[(MoO_2)_4O_3(Hcit)_2](H_2O)_6$ also have a similar tridentate chelation mode. Furthermore, such tridentate chelation has been reported for nickel(II),[17a] iron(II),[17a] magnesium(II),[17b] and manganese(II)[17c] citrate complexes. Accordingly, it is likely that the present tridentate chelation formed by two carboxylic groups (one central, one terminal) and one hydroxy group is the most common for citrate binding to metal ions, irrespective of the actual charge on the citrate (Hcit^{3-} or cit^{4-}). Apparently the tridentate chelating character of the citrate ligand is quite general, probably also in solution (vide infra).

Solution Behavior at Low Concentration (Less Than 20 mM Bi). In order to understand solution structures and to relate these to the obtained solid compounds, ^1H and ^{13}C NMR spectra were measured. Figure 6 shows ^1H NMR spectra of compound **1** at three different pH* values. The three spectra show an AB pattern assignable to CH_2 groups of citrates with no other peaks. It means that all citrates in the solutions are averaged on the NMR time scale. Furthermore, the chemical shifts and the peak widths are

Table V. Important Coordination Bond Lengths (Å) and Bond Angles (deg) of the Non-Hydrogen Atoms of $(NH_4)_4[Bi(cit)(Hcit)(H_2O)_2](H_2O)$ (**5**)

Bi1–Bi1[a]	5.9720 (6)	Bi1–O211	2.746 (5)
Bi1–O111	2.526 (5)	Bi1–O41	2.790 (7)
Bi1–O131	2.136 (5)	Bi1–O42	2.925 (7)
Bi1–O162	2.348 (6)	Bi1–O151[a]	2.362 (5)
Bi1–O212	2.448 (5)	Bi1–O152[a]	2.868 (5)
O111–Bi1–O131	75.3 (2)	O162–Bi1–O42	132.1 (2)
O111–Bi1–O162	74.3 (2)	O162–Bi1–O151[a]	89.6 (2)
O111–Bi1–O212	112.6 (2)	O162–Bi1–O152[a]	70.7 (2)
O111–Bi1–O211	71.5 (2)	O212–Bi1–O211	49.8 (2)
O111–Bi1–O41	68.2 (2)	O212–Bi1–O41	133.0 (2)
O111–Bi1–O42	128.0 (2)	O212–Bi1–O42	71.4 (2)
O111–Bi1–O151[a]	157.0 (2)	O212–Bi1–O151[a]	72.3 (2)
O111–Bi1–O152[a]	134.4 (2)	O212–Bi1–O152[a]	112.7 (2)
O131–Bi1–O162	72.9 (2)	O151–Bi1–O211	120.9 (2)
O131–Bi1–O212	77.0 (2)	O151–Bi1–O152[a]	49.0 (2)
O131–Bi1–O211	92.4 (2)	O211–Bi1–O41	92.2 (2)
O131–Bi1–O41	139.6 (2)	O211–Bi1–O152[a]	141.3 (2)
O131–Bi1–O42	146.2 (2)	O211–Bi1–O42	76.3 (2)
O131–Bi1–O151[a]	84.4 (2)	O41–Bi1–O42	73.4 (2)
O131–Bi1–O152[a]	119.3 (2)	O41–Bi1–O151[a]	126.1 (2)
O162–Bi1–O212	146.2 (2)	O41–Bi1–O152[a]	78.1 (2)
O162–Bi1–O211	145.2 (2)	O42–Bi1–O151[a]	75.0 (2)
O162–Bi1–O41	80.8 (2)	O42–Bi1–O152[a]	65.0 (3)

[a] $1.0 - x$, $1.0 - y$, $1.0 - z$.

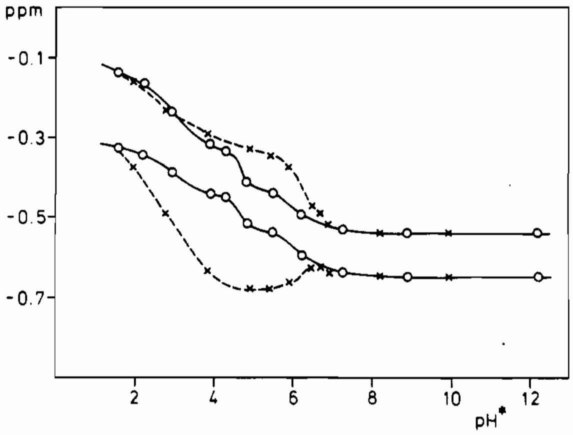

Figure 7. pH dependence of the chemical shifts of methylene protons in a citrate: (×) compound **1** (15 mM citrate); (○) H_4cit (15 mM citrate).

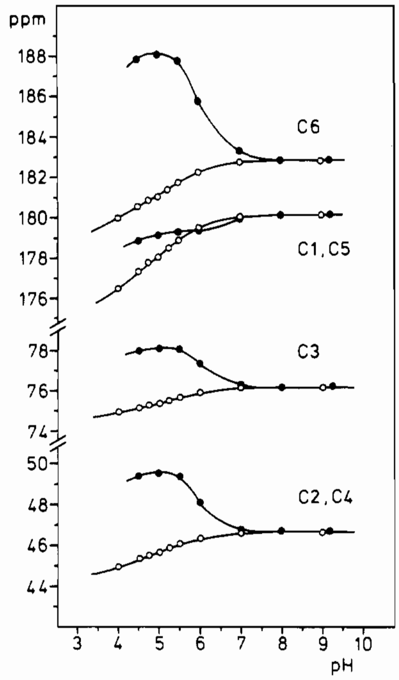

Figure 8. pH dependence of the chemical shifts of four independent carbon atoms in a citrate: (●) compound **1** (50 mM citrate); (○) H_4cit (50 mM citrate).

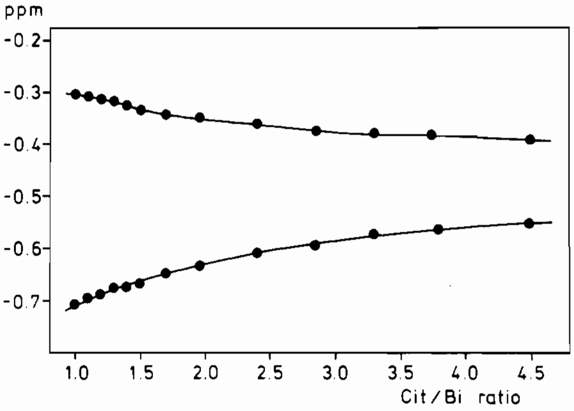

Figure 9. Change of chemical shifts of methylene protons in a citrate as a function of the molar ratio (citrate/Bi) at pH* 5.0.

pH dependent. The chemical shifts are plotted as a function of pH* in Figure 7 for solutions containing compound **1** and free H_4cit. Above pH* 7, the chemical shifts of the compound are practically the same as those of the free citrate. The results of pH titration and peak narrowing observed at higher pH regions (see Figure 6a) suggest that under basic conditions citrates are hardly, if at all, coordinated to Bi(III). Results of ^{13}C NMR spectra are in favor of this suggestion. As shown in Figure 8, chemical shifts of four independent carbons, i.e. terminal (C1, C5) and central (C6) carboxylate groups, methylene carbons (C2, C4), and a quaternary carbon (C3), are practically the same as those of a free citrate. Furthermore, above pH 7 peak narrowing occurs just as found in the ^1H NMR spectra (for citrate numbering, see Figure 10). As Figure 7 shows, chemical shifts of methylene protons of compound **1** come the closer at the lower pH*. However, it cannot merely be due to uncoordination as the case at higher pH regions, since below pH* 2.85 a white finely divided powder, which should be a mixture of bismuth citrate and bismuth oxychloride,[5] precipitates. Hence, the resulting solutions have a bismuth:citrate ratio less than 2:3. As described below, the chemical shifts of the citrate (^1H and ^{13}C) atoms depend on bismuth:citrate ratios. Thus, even in lower pH regions citrates seem to coordinate to Bi(III) with rapid ligand exchanging. In the solid state, it is found that in fact only the central carboxyl group ionizes first. X-ray analyses of anhydrous sodium and lithium dihydrogen citrates, which are isomorphous, show that only the central carboxyl group ionizes.[19a] Next the two terminal carboxyl groups follow, and finally the hydroxyl group ionizes.[19b] NMR studies have indicated that this order of ionization is generally found in solution as well.[20] In aqueous solutions bismuth(III), being a class B metal, is unlikely to hold rigid chelate structures with citrates, such as seen in the solid compounds. In fact, the AB patterns observed for ^1H NMR spectra indicate destruction of the rigid chelation and the presence of rapid ligand exchange. In Figure 8, chemical shifts of ^{13}C NMR spectra are plotted as a function of pH for the compound and free citrate. Differences in chemical shifts of central carboxylate between the compound and free citrate are much larger than those of the terminal one, suggesting that, around pH* 3–6, citrates may be coordinated mainly through the central carboxylate to Bi(III).

After addition of free citrate to solutions containing compound **1**, ^1H NMR spectra of the resultant solutions give no other peaks besides the AB pattern. This clearly indicates that the ligand exchange is more rapid than the NMR time scale. In Figure 9 the chemical shifts of the methylene protons are plotted against

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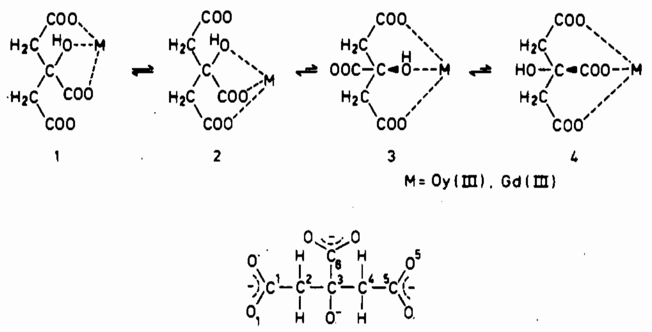

Figure 10. Schematic structures of the four binding modes found for binding of Ln(III) ions to citrate.

the citrate:Bi ratio. As expected from the rapid ligand exchange, the chemical shifts depend on the ratio and the shifts move toward that of free citrate with increase in the ratio. The compounds obtained (**1**, **2a**, **2b**, **3a**, and **5**) show only an AB pattern in their ^{1}H NMR spectra. Furthermore, the rapid ligand exchange is evident from the fact that the chemical shifts of these compounds measured at pH* 5 are essentially the same as those predicted from Figure 9.

So far, several NMR studies on metal citrate complexes have been reported, e.g. for $U^{II}O_2$,[21] V(V),[22] Dy(III),[23] Ga(III),[24] Al(III),[25] W(VI),[26] Gd(III),[27] etc. In general, in these cases separate signals are observed for free and bound citrates, because of slow ligand exchange on the NMR time scale, except for the cases of Dy(III)[23] and Gd(III).[27] For these latter two metal citrate compounds rapid ligand exchange was explained by a fast equilibrium between the four species (1–4) (Figure 10), in which 1 and 2 were considered to be the main species. In the main species 1 and 2, the citrate functions as a tridentate chelate ligand, just as seen in the tetraionized citrate (cit^{4-}) of the compounds **1** and **5** in their solid state. However, the citrate present in the solutions was considered to be a triionized one ($Hcit^{3-}$) with a hydronated alcohol group. In view of the resemblance in the rapid ligand exchange and coordination number of 9 between Bi(III) and Ln(III), it is likely that a fast equilibrium as seen in the Dy(III) and Gd(III) solutions occurs in a bismuth citrate system. In fact, as shown in Figure 8, chemical shift changes in C2 (=C4) and C3 upon coordination are quite large and not negligible, not even for the terminal carboxylate.

Solution Behavior at High Concentration (More Than 50 mM Bi). All bismuth citrate compounds obtained are slightly soluble in water, except for compound **5**. However, all the compounds have extremely high solubility under alkaline conditions (i.e. at pH > 8). The ^{13}C NMR spectrum of **1** at pH 9.00 is redrawn in Figure 11. The main peaks have practically the same chemical shifts as those of free citrate. In addition, compounds **2**, **3**, and **5** give similar NMR features, i.e. with main peaks assignable to uncoordinated citrates and with some extra peaks assignable to coordinated citrates, and although the intensity of the latter peaks depends on concentrations, the former chemical shifts are practically the same as those of compound **1**. This would be predicted from the results mentioned above, since citrates are hardly, if at all, coordinated to Bi(III) above pH 7. Extra peaks near the main peaks are undoubtedly due to coordinated citrates, and their intensities increase with increasing concentration as shown in Figure 11.

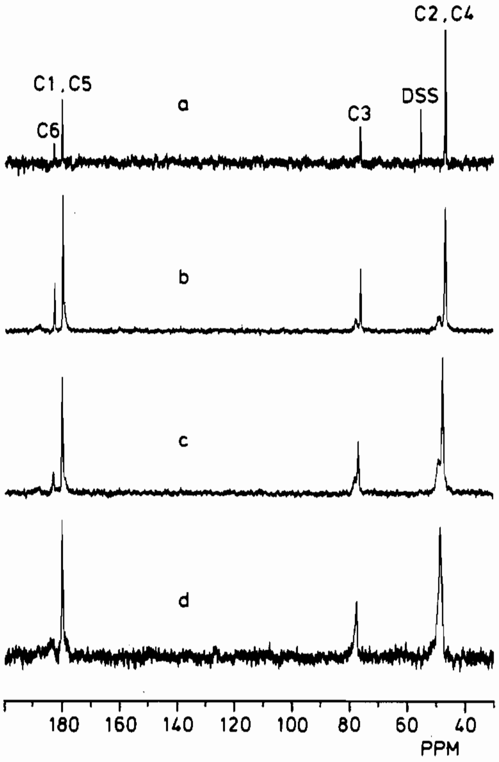

Figure 11. ^{13}C NMR spectra of compound **1** in H_2O at pH 9.0: (a) 50 mM citrate, at 25 °C; (b) 1.0 M citrate, at 10 °C; (c) 1.0 M citrate, at 40 °C; (d) 1.0 M citrate, at 70 °C.

Many examples[21,22,24–26] have been reported on metal citrate compounds having polynuclear structures both in the solid state and in solution. Under high concentration conditions, a part of the bismuth is likely to form a polymeric structure, just as seen in the solid products. ^{13}C NMR spectra measured under high-concentration conditions also depend on the temperature. As shown in Figure 11, coalescence of the main and the extra peaks is observed, indicating that at higher temperatures the polymeric units decompose and that all citrates become averaged on the NMR time scale (fast exchange).

Solution Behavior of Compounds 4a and 4b. Both compounds show anomalous behavior in their solubility. Although the compounds are insoluble in water in low concentrations (e.g. 6.00 mg of **4a**/mL in H_2O, corresponding to 5 mM for a $[(BiO)_2Bi(cit)_2]^{3-}$ unit), they are quite soluble in higher concentrations (e.g. 118 mg/mL in H_2O, corresponding to 100 mM). Once dissolved, the solution does not yield any precipitation (even after dilution). Further, compounds of this type become soluble in the presence of added citrate, even in low concentrations. The ^{1}H NMR spectrum of **4a** measured at pH* 6.96 (118 mg/mL in D_2O) is very complicated (the spectrum is given in Figure S1, as supplementary material). It shows many extra peaks, besides an AB pattern, which are independent of time (at least for periods of more than 2 weeks). However, the spectrum depends on the concentration used. When the concentrated solution, whose pH* was adjusted to 6.96 prior to its addition, is diluted to 5 mM with D_2O, the extra peaks decrease to less than one-third of the original intensity and, in addition, the pH* value of the solution rapidly increases to 7.21, suggesting that the extra peaks originate from coordinated citrates and that parts of the citrates are released. The extra peaks observed at pH* 6.96 (5 mM in D_2O) disappear at higher pH (=8.00). After measurement at pH* 8.00, the sample does not show the extra peaks at pH* 6.96.

Finally, when solutions of free citrate that have the same pH* value (=6.96) are added, the extra peaks vanish and the pH* values of the resultant solutions rapidly increase.[28] These results

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clearly indicate that the extra peaks originate from coordinated citrates and that the citrates are released to be averaged on the NMR time scale, when a sufficient amount of citrate (cit:Bi > 1:1) is present in the system. In fact, for the all other bismuth citrate compounds (**1**, **2a**, **2b**, **3a**, and **5**) whose citrate:bismuth ratios are higher than 1.0, all citrates average on the NMR time scale under low-concentration conditions, as mentioned above.

According to the elemental analyses, **4a** and **4b** seem to contain $[Bi-O(H)-Bi]_n$ units. The hydrolysis of Bi(III) has been extensively studied and the predominance of several hexanuclear species, such as $[Bi_6O_4(OH)_4]^{6+}$, in acidic solutions is well established.[29,30] If the presence of such hexanuclear species is assumed for the solutions of **4a** and **4b**, then the behavior can be explained well. Since the hexanuclear unit decomposes in basic conditions, the "isolated" bismuth ions will be able to react with citrates, which exchange rapidly on the NMR time scale just like the other bismuth citrate compounds. An excess of citrate may coordinate with such a unit, so as to weaken and destroy the Bi–O bonds that are frameworks in a hexanuclear cluster. Although the structure determination of compound **4** as a solid has been attempted, this was unsuccessful so far, due to the poor quality of the crystals.

Concluding Remarks

In this investigation, five types of solid compounds were synthesized by varying the $Bi:H_4cit:KOH:NH_4OH$ ratio. In the case of two compounds, i.e. **1** and **5**, a 3-D structure could be determined by using X-ray diffraction on single crystals. For the citrate anion, whether in triionized or tetraionized form, tridentate chelation to Bi(III) is evident. Only in the case of compound **4**, prepared with a small excess of citrate, are not all Bi ions tridentately chelated by citrate (ratio Bi:citrate = 3:2), and a cluster structure, such as $[Bi_6O_4(OH)_4(Hcit)_4]^{6-}$, appears likely.

To the best of our knowledge, the rapid ligand exchange of citrates is unprecedented for bismuth. On the other hand, in solutions with high concentration that are attained only under basic conditions, citrates coordinate to bismuth rigidly, to yield oligomeric or polymeric units. Exceptionally, compounds **4a** and **4b** show separate signals for free and coordinated citrates in their ^1H NMR spectra even in low concentration. Although the reason is not clear at this stage, a plausible explanation is given by existence of $[Bi-O(H)-Bi]_n$ units in the solid form. The most plausible candidate for the unit is a well-established hexanuclear cluster $[Bi_6O_4(OH)_4]^{6+}$.[27,28] In that case compound **4** should be described as $(NH_4)_xK_{6-x}[Bi_6O_4(OH)_4(Hcit)_4](H_2O)_8$ in the solid state.

Note Added in Proof. After the acceptance of this paper, a communication has appeared in this journal,[33] dealing with the crystal structure of $KBi(C_6H_4O_7)\cdot 3H_2O$, $(KBi(cit^{4-})\cdot 3H_2O)$ a compound close in analyses (though not identical) to our compounds **2** and **3**. Although these authors used ammonia for growth of the crystals, they did not give a K/NH_4 ratio. The structure of their compound also contains the Bi(cit) units in which cit^{4-} is tridentate chelating to Bi(III), with a short Bi–O3 distance, just as found in our compounds **1** and **5**. No Bi–Bi distances were given.

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Registry No. **5**, 136445-28-8; KBi(cit), 136445-27-7.

Supplementary Material Available: A figure showing the NMR spectrum of compound **4a** and tables of bond lengths and bond angles, of fractional coordinates of the hydrogen atoms, and of anisotropic thermal parameters of the non-hydrogen atoms (13 pages); listings of structure factors (67 pages). Ordering information is given on any current masthead page.

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(28) As the citrate:bismuth ratio increases, the pH* value increases. Resultant pH* values for each citrate:bismuth ratio are as follows: pH* 6.96 for cit:Bi = 2:3 (without addition of free citrate), pH* 7.18 for 3:3, pH* 7.25 for 4:3, pH* 7.29 for 5:3, and pH* 7.31 for 6:3.

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Ethylene, Silene, and Disilene Coordinate Bonds with Platinum(0) and Platinum(II). An ab Initio MO/MP4 and SD–CI Study

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$[PtCl_3L]^-$ and $Pt(PH_3)_2L$ ($L = C_2H_4$, SiH_2CH_2, or Si_2H_4) are investigated with ab initio MO/MP4 and SD–CI methods. Binding energies of these complexes increase in the order ethylene < silene < disilene in both Pt(0) and Pt(II) complexes, and their coordinate bonds are stronger in Pt(II) complexes than in Pt(0) complexes. The disilene coordinate bond of $Pt(PH_3)_2(Si_2H_4)$ can be described as a three-centered metallocyclopropane type interaction, while the ethylene coordinate bond of $[PtCl_3(C_2H_4)]^-$ and $Pt(PH_3)_2(C_2H_4)$ exhibits the character of C=C double-bond coordination. Electron correlation has little effect on geometries of these complexes but has a significant influence on binding energies.

Introduction

Transition-metal complexes with silene and disilene are of considerable interest in the chemistry of Si compounds[2] because coordination to transition metals is one useful way to stabilize such reactive species as silene and disilene. In this regard, several transition-metal complexes of silene and disilene have been reported in recent studies.[3] However, very little has been known regarding the coordinate bond nature and the electronic structure of transition-metal complexes of silene and disilene, and only one theoretical study of a disilene complex has been reported,[4] to our knowledge.

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