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Structural Investigations of Calcium-Binding Molecules. 4. Calcium Binding to Aminocarboxylates. Crystal Structures of Ca(CaEDTA)·7H_2O and Na(CaNTA)[1]

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The structural characteristics of calcium ion binding to the aminocarboxylates ethylenediaminetetraacetate (EDTA) and nitrilotriacetate (NTA) have been studied by single-crystal X-ray crystallography. In the two crystalline complexes studied, Ca(CaEDTA)·7H_2O and Na(CaNTA), the full chelating power of the aminocarboxylate ligand is observed and the primary coordination environment of the calcium ion contains additional occupied sites. Ca(CaEDTA)·7H_2O crystallizes in the triclinic space group $P\bar{1}$ with a = 9.916 (2) Å, b = 10.175 (2) Å, c = 11.192 (2) Å, α = 102.64 (1)°, β = 103.50 (1)°, γ = 106.52 (1)°, and Z = 2. The compound can best be described as the calcium salt of a $CaEDTA^{2-}$ complex in which the Ca^{2+} has eightfold coordination with a hexadentate EDTA ligand. Na(CaNTA) crystallizes in the cubic space group $P2_13$ with a = 9.626 (2) Å and Z = 4. In the $CaNTA^-$ complex the Ca^{2+} has sevenfold coordination with a tetradentate NTA ligand.

Introduction

The aminocarboxylates ethylenediaminetetraacetate (EDTA) and nitrilotriacetate (NTA) have been long known and studied as calcium-binding agents, not only with respect to practical applications but also as classic research models for polydentate chelation. The commercial uses of EDTA as a sequestrant of Ca^{2+} and other metal ions are widespread and well documented in the trade and applied research literature.[2] NTA, also, because of its ability to effectively sequester Ca^{2+}, has been actively considered and has achieved limited usage as a replacement for phosphates in household and industrial cleaning products.[3]

The Ca^{2+}-binding properties of EDTA and NTA in aqueous solutions have been extensively studied.[4] The potential for polydentate binding by these ligands, hexadentate for EDTA and tetradentate for NTA, when complexed with Ca^{2+} is well-known. The total coordination environment of $CaEDTA^{2-}$ and $CaNTA^-$ complexes is less well-known. Very often the $CaEDTA^{2-}$ complex is represented as hexadentate and generally with idealized octahedral (O_h) coordination about the calcium ion. However, the extensive X-ray structural studies of Hoard and his co-workers have indicated that such a complex of a relatively large cation like Ca^{2+} should have a coordination number greater than 6.[5] In fact, Hoard and Cohen[6] predicted that a hexadentate EDTA chelate of calcium ion is expected to have a coordination geometry much like that of the EDTA chelates of the rare earth ions which are hexadentate and have water molecules occupying additional coordination sites. For similar reasons a multidentate ligand such as NTA should form Ca^{2+} complexes with coodination numbers greater than 6. In recent years X-ray structural studies of crystalline complexes of Ca^{2+} and multidentate organic ligands have commonly revealed coordination numbers larger than 6 for calcium.[7,8]

To our knowledge there have been no reported X-ray structural studies of calcium complexes of EDTA.[23] A study of CaHNTA was reported by Whitlow;[10] however, due to the incomplete ionization of the ligand it was not possible to study the mulidentate capabilities of NTA as a calcium-binding ligand. Because these ligands are so well-known and prototypical in the area of calcium binding, the structures reported here of crystalline calcium EDTA and NTA complexes were deemed of considerable importance.

Experimental Section

Ca(CaEDTA)·7H_2O. A solution of 0.33 M calcium acetate and 0.16 M H_4EDTA was adjusted to pH 9 with tetramethylammonium hydroxide. After the solution was filtered through a 20-μm frit, the solution was allowed to evaporate over 3–4 days at ambient conditions. Colorless, irregularly shaped parallelepipeds were obtained. Elemental analysis was consistent with the given stoichiometry.

Table I. Crystal Data

	Ca(CaEDTA)·7H_2O		Na(CaNTA)
formula	$C_{10}H_{12}N_2O_8{}^{4-}$, $2Ca^{2+}$, 7H_2O		$C_6H_6NO_6{}^{3-}Ca^{2+}$, Na^+
fw	494.48		251.12
space group	$C\bar{1}$	$C^1{}_iP\bar{1}$ (No.2)	T^4, $P2_13$ (No. 198)
cell constants[a]			
a, Å	16.692 (3)	9.916 (2)	9.626 (2)
b, Å	13.378 (2)	10.175 (2)	
c, Å	9.916 (2)	11.192 (2)	
α, deg	114.31 (1)	102.64 (1)	
β, deg	90.96 (1)	103.50 (1)	
γ, deg	95.59 (1)	106.52 (1)	
V, Å^3	2004.4	1002.2	891.9
F(000)	1040	520	512
μ, cm^{-1}	6.3		7.4
d(obsd), g/cm^3	1.64		not measured
d(calcd), g/cm^3	1.63		1.87
Z, formula units/cell	4	2	4
total independent reflctns	3549		318
$I > 2\sigma(I)$	2866		287
$I < 2\sigma(I)$	683		31
R_1, R_2	0.077, 0.10		0.038, 0.025
R_1, R_2 including $I < 2\sigma$	0.087, 0.10		0.045, 0.025
crystal size, cm	0.01 × 0.05 × 0.04[b]		0.025 × 0.025 × 0.025

[a] Ambient temperature, ~22 °C. [b] Estimated because crystal used in data collection decomposed before size could be measured accurately.

Anal. Calcd for Ca_2EDTA·7H_2O: C, 24.3; H, 5.3; N, 5.7; Ca, 16.2. Found: C, 24.9; H, 4.6; N, 5.8; Ca, 14.8.

Na(CaNTA). A solution of 0.35 M sodium silicate and 0.5 M Na_3NTA was adjusted to pH 4.5 with acetic acid and then allowed to form a gel at 45 °C for 12 h. After 2 weeks of contact between the gel and a 0.1-M solution of $CaCl_2$, clear colorless tetrahedral crystals of Na(CaNTA) began to form. The compositional analysis was obtained from the crystallographic results.

Crystallographic Data

Determination of Space Groups and Lattice Parameters. Preliminary X-ray investigations revealed the diffraction symmetries to be triclinic for Ca(CaEDTA) and cubic for Na(CaNTA). The systematic absences and the Laue group for Na(CaNTA) are consistent with the uniquely defined space group $P2_13$. Space group $P\bar{1}$ for Ca(CaEDTA) was confirmed by the solution and refinement of the structure. Cell dimensions, given in Table I, were obtained by least-squares refinement of three instrument angles for 15 general high-angle reflections. The instrument angles were measured with

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Mo Kα (λ 0.709 26 Å) radiation by using a Syntex four-circle diffractometer that was equipped with a graphite monochromator ($2\theta_m$ = 12.16° at $t \sim 22$ °C).

Collection and Reduction of Intensity Data. Three-dimensional single-crystal intensity data (Mo Kα radiation) were collected by the θ–2θ technique. Variable scan rates (2–15°/min) were chosen, so that the less intense reflections could be scanned slower to improve their counting statistics. Individual background measurements were made at the end points of the scan range, each for a time of half the scan time. In both data sets reflections were monitored periodically and in both cases there was only random fluctuation (maxima of 3% for Ca(CaEDTA) and 2% for Na(CaNTA)) of the intensities for these reflections (004, 601, 061 for Ca(CaEDTA); 200, 020, 002, 11$\bar{1}$ for Na(CaNTA)). Lorentz and polarization corrections were applied, but no absorption correction was made. Standard deviations of the observed structure factor amplitudes were based solely on counting statistics. Only those reflections whose intensities were greater than 2σ were used in the solution and refinement of the structures.

Solution and Refinement of the Structures. Ca(CaEDTA)·7H$_2$O. Solution of the structure was accomplished by obtaining the two calcium ion positions from a sharpened Patterson map. A Fourier map, which was calculated with phases based on the two calcium ion positions, revealed the nonhydrogen atoms of the complex and four of the seven water molecules. A subsequent difference Fourier map contained peaks for the remaining water molecules, but these peaks were diffuse, suggesting that these atoms are probably disordered. (A refinement of the structure in $P1$ led to large variations ($\sim$0.15 Å) in chemically equivalent C–C and C–N bond lengths, so we concluded that the true space group is $P\bar{1}$ and the water molecules are disordered.)

Least-squares refinement for five cycles of positions and isotropic temperature factors gave an R of 0.10; the occupancies for the three disordered water molecules were established during the initial stages of least-squares refinement by holding their temperature factors constant. All atoms except the seven water oxygen atoms were converted to anisotropic temperature factors and the least-squares refinement reduced the R value to 0.084 in three cycles. An additional four cycles of least-squares calculations, where all positional parameters, all temperature factors, and an overall scale factor were varied, served to complete the refinement to an R value of 0.077. Shifts in the final full-matrix least-squares cycle were less than 0.2σ for all parameters. A final difference density map contained only a randomly fluctuating background below ±0.5 e/Å^3. Of the 12 largest peaks ($\sim$0.5 e/Å^3) in the final difference map, all are in the vicinity of the disordered water molecules, so that the disorder, rather than partial occupancy, appears to be real. Difference Fourier maps were inspected throughout the refinement process for any pattern in the presumably disordered water molecules; no systematic pattern was evident. Positional parameters were estimated for EDTA hydrogen atoms and were included in the final structure factor calculations, but they were not refined. Weights equal to $1/\sigma^2(|F_o|)$ were utilized in the least-squares calculations.

Final atomic parameters are given in Table II and supplementary material Table A-I and are with respect to the $C\bar{1}$ unit cell described in Table I. The estimated standard deviations were calculated from the inverse of the final full-matrix least-squares cycle. The final R value for these parameters was 0.077 (0.10 for weighted R) for the observed reflections only.

Na(CaNTA). Solution of the structure by conventional Patterson methods was unsuccessful because initially the presence of the sodium ion was unsuspected. The most probable solution produced by MULTAN[11] contained the complete structure of nonhydrogen atoms. The initial attempt of assigning sodium to the remaining counterion proved successful.

Table II. Final Positional Parameters and Isotropic Temperature Factors for the Water Molecules and the Hydrogen Atoms in Ca(CaEDTA)·7H$_2$O[a]

	x	y	z	B, Å^2
Ca1	0.46293 (12)	0.65082 (14)	0.12337 (20)	
Ca2	0.49557 (11)	0.15505 (14)	0.14932 (20)	
O1	0.4834 (4)	0.4785 (5)	0.1230 (7)	
O2	0.5091 (4)	0.3144 (5)	0.0983 (7)	
O3	0.3594 (4)	0.0970 (5)	0.0565 (7)	
O4	0.2289 (4)	0.1177 (5)	0.0619 (9)	
O5	0.5751 (4)	0.3094 (5)	0.6314 (7)	
O6	0.5632 (4)	0.2682 (5)	0.3890 (7)	
O7	0.4887 (4)	−0.0380 (5)	0.1216 (7)	
O8	0.4317 (4)	−0.1708 (5)	0.1820 (8)	
N1	0.3950 (5)	0.3083 (6)	0.2886 (8)	
N2	0.4231 (4)	0.1217 (5)	0.3624 (8)	
C1	0.3769 (6)	0.3088 (7)	0.4346 (10)	
C2	0.3578 (6)	0.1926 (7)	0.4220 (10)	
C3	0.4336 (6)	0.4148 (7)	0.3034 (10)	
C4	0.4782 (6)	0.4027 (8)	0.1657 (10)	
C5	0.3200 (6)	0.2778 (8)	0.1914 (11)	
C6	0.3009 (6)	0.1540 (8)	0.0956 (10)	
C7	0.4896 (6)	0.1477 (7)	0.4769 (10)	
C8	0.5457 (6)	0.2512 (7)	0.5018 (10)	
C9	0.3907 (6)	0.0051 (7)	0.3081 (10)	
C10	0.4426 (6)	−0.0743 (7)	0.1960 (10)	
O9	0.3295 (5)	0.5919 (7)	0.0200 (10)	4.91 (20)
O10	0.6390 (4)	0.1234 (5)	0.1278 (7)	2.76 (14)
O11	0.6008 (4)	0.7176 (5)	0.1884 (8)	2.98 (15)
O12	0.6383 (5)	−0.0570 (7)	0.2854 (9)	4.54 (19)
O13*	0.7434 (10)	0.2990 (14)	0.1167 (20)	5.7 (4)
O14*	0.6775 (10)	0.4138 (14)	0.3376 (19)	7.1 (4)
O15*	0.7573 (8)	0.1324 (11)	0.3707 (15)	5.6 (3)
H1A	0.3305	0.3525	0.4751	5.5
H1B	0.4257	0.3460	0.5073	5.5
H2A	0.3074	0.1570	0.3543	5.5
H2B	0.3458	0.1944	0.5229	5.5
H3A	0.4738	0.4466	0.3935	5.5
H3B	0.3922	0.4678	0.3209	5.5
H5A	0.3245	0.3182	0.1244	5.5
H5B	0.2729	0.3041	0.2553	5.5
H7A	0.5223	0.0824	0.4465	5.5
H7B	0.4653	0.1564	0.5736	5.5
H9A	0.3876	−0.0150	0.3970	5.5
H9B	0.3353	−0.0060	0.2625	5.5

[a] Estimated standard deviations in the last digit are given in parentheses. [b] The occupancy fractions of these atoms are O13 = 0.52, O14 = 0.61, and O15 = 0.66.

Table III. Final Atomic Positions and Hydrogen Temperature Factors of Na(CaNTA)[a]

	x	y	z	B, Å^2
Ca	0.16182 (11)			
Na	0.67172 (22)			
O1	0.5987 (4)	0.2898 (4)	0.0736 (4)	
O2	0.3772 (4)	0.2244 (4)	0.0615 (4)	
N	0.3195 (4)			
C1	0.4653 (6)	0.2916 (7)	0.2813 (7)	
C2	0.4816 (6)	0.2687 (6)	0.1255 (6)	
H1A	0.500 (6)	0.201 (6)	0.325 (7)	5.4 (20)
H1B	0.542 (5)	0.369 (5)	0.316 (5)	2.3 (12)

[a] Estimated standard deviations are given in parentheses for the last digit.

Least-squares refinement for three cycles of positions and isotropic temperature factors gave an R value of 0.063. The thermal parameters of all atoms were converted to anisotropic temperature factors with the threefold-symmetry constraints placed on Ca, Na, and N temperature factors, and the refinement reduced the R value to 0.050 in three cycles. A difference Fourier map contained only two peaks, both corresponding to chemically reasonable positions for the two independent hydrogen atoms. An additional four cycles of least-squares calculations, where all independent positional parameters, hydrogen isotropic temperature factors, nonhydrogen anisotropic temperature factors, and an overall scale factor were varied, served to complete the refinement at an R value of 0.039. Shifts in the final full-matrix least squares were less than 0.1σ for all parameters. A final difference density map contained only a randomly fluctuating background below ±0.3 e/Å^3. Weights equal to $1/\sigma^2(|F_o|)$ were employed in the least-squares calculations.

Final atomic parameters are given in Tables III and supplementary material Table A-II. The estimated standard deviations were calculated from the inverse of the final full-matrix least-squares cycles. The final R value for these parameters was 0.039 (0.047 for weighted R) for the observed reflections only.

All calculations for both structures were performed on a Data General Nova 1200 computer with standard crystallographic programs

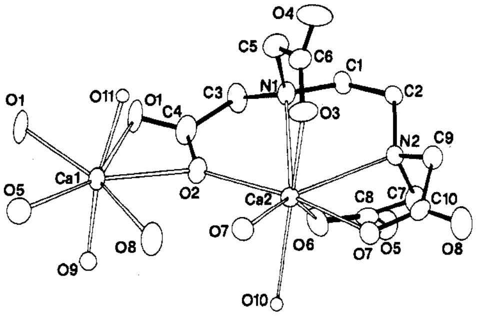

Figure 1. Coordination and ligand geometry for Ca(CaEDTA). Only the water molecules that are involved in coordination are included. No hydrogen atoms are included.

Table IV. Hydrogen-Bonding Network in Ca(CaEDTA)·$7H_2O$

	dist, Å	symmetry information			
O9···O4	2.65 (1)	t[a]	1/4	1/4	0
···O13	2.71 (2)	t	1/2	1/2	0
O10···O3	2.76 (1)	t	1/2	0	0
···O6	2.92 (1)				
···O13	2.83 (2)				
O11···O4	2.68 (1)	t	1	1	0
···O12	2.76 (1)			$1 + y$	
O12···O11	2.76 (1)			$1 + y$	
···O15	2.88 (2)				
O13···O9	2.71 (2)	t	1/2	1/2	0
···O10	2.83 (2)				
···O13	2.17 (2)	t	3/4	1/4	0
···O14	2.45 (2)				
O14···O6	2.80 (2)				
···O13	2.45 (2)				
O15···O5	2.83 (2)	t	3/4	1/4	1/2
···O12	2.88 (2)				

[a] t refers to translation symmetry.

that were modified for the Nova 1200 by Syntex Analytical Instruments. Least-squares methods were performed by full-matrix methods. Atomic scattering factors were those of Stewart, Davidson, and Simpson[12] for hydrogen and Cromer[13] for the remaining atoms.

Description of the Structures

Ca(CaEDTA)·$7H_2O$. The crystal structure of Ca(CaEDTA)·$7H_2O$ consists of an intricate network of ligand-bridged coordination complexes and hydrogen bonds, such that no discrete complexes exist. Figure 1 illustrates the coordination about the two independent calcium ions and depicts the subunit that forms a planar network of ligand-bridged calcium ions. The inversion centers in the $x = 0$ and $x = {}^1/_2$ planes extend this network parallel to the *bc* plane. Between the layers of calcium ions, four water molecules of crystallization form hydrogen bonds which hold the structure together in the third dimension. The disorder in three of these water molecules, which we have observed in two independent crystal investigations, seems inherent in crystals of this compound. The three remaining water molecules participate in and complete the coordination polyhedra about the calcium ions. Distances and angles for the hydrogen-bonding network are described in Table IV.

Like many of the dication complexes of EDTA, this dicalcium complex can be considered as the calcium salt of a $CaEDTA^{2-}$ complex. The EDTA ligand binds as a hexadentate ligand to Ca2; four symmetry-related Ca1 ions are bound to the EDTA ligand. Three of the Ca1 ions are bound in a monodentate fashion by the EDTA ligand and one is bound in a bidentate fashion. In this manner Ca1 cations, along with the waters of hydration, serve to bridge the $CaEDTA^{2-}$ complexes together.

For Ca1 the coordination number is 7 and the coordination polyhedron is approximately pentagonal bipyramidal. In the pentagonal plane of Ca1 the coordination sites are occupied by single oxygen atoms (O1, O1′, O2, O5, O8) from four different but symmetry-related EDTA ligands; two of these equatorial positions are occupied by a bidentate carboxylate group (O1 and O2). The two axial sites are filled by water molecules (O9 and O11).

Table V. Cation Coordination

	Ca(CaEDTA)·$7H_2O$		
Ca1–O1	2.362 (8)	Ca2–O2	2.378 (7)
Ca1–O1′	2.581 (7)	Ca2–O3	2.370 (7)
Ca1–O2′	2.469 (7)	Ca2–O6	2.414 (7)
Ca1–O5′	2.377 (7)	Ca2–O7	2.473 (7)
Ca1–O8′	2.327 (8)	Ca2–O7′	2.526 (6)
Ca1–O9′	2.355 (9)	Ca2–O10	2.470 (7)
Ca1–O11	2.363 (7)	Ca2–N1	2.711 (8)
		Ca2–N2	2.623 (7)
	Na(CaNTA)		
Ca–N	2.629 (2)	Na–O1	2.431 (4)
Ca–O1	2.392 (4)	Na–O2	2.349 (4)
Ca–O2	2.365 (4)		

For the EDTA-chelated Ca2 the coordination number is 8 and the coordination polyhedron is approximately square antipyrismatic. Two sites, in addition to the six occupied by the hexadentate EDTA ligand, are filled by the water molecule (O10) and a symmetry-related EDTA oxygen atom (O7). Three coordination sites of each square plane are related by an approximate twofold axis through the ethylene bridge of EDTA (see Figure 1). Operation by this approximate twofold axis interchanges O10 and O7′. More precise descriptions of the cation environments can be obtained from the interatomic distances and angles in Tables V and VI.

The conformation of the EDTA ligand in this complex is similar to that of the free acid.[14] When the hexadentate chelation of this ligand is fully utilized, as it is in this structure, the geometry of the ligand can be described by the conformation of the five-membered rings.[15,16] The four glycinate rings are fused either axially or equatorially to a central ethylenediamine ring and the calcium ion Ca2 is common to each ring. In Table VI, the ligand conformation has been characterized by the interatomic distances and angles and torsional angles. These values are similar to those corresponding values found in the conformational studies of several EDTA complexes.[15,16] The torsional angles in the rings are typical of a half-chair conformation.[17]

Na(CaNTA). The crystal structure of Na(CaNTA) can be described as that of the sodium salt of $CaNTA^-$. $CaNTA^-$ complexes are linked together in an infinite network by oxygen-bridging Na^+ ions and by nonchelating oxygen atoms which fill out the coordination sphere of the Ca^{2+} ions (see Figure 2). No discrete complexes exist. It is unusual for a Ca^{2+} complex crystallized from an aqueous environment to form an anhydrous compound such as this. Indeed we have observed this crystalline form over a wide pH range. The high crystal symmetry is, we believe, the reason for the stability of the anhydrous form. This same crystalline form has even been observed as an excreted form of NTA in animal studies.[18]

The sevenfold coordination (see Figure 3) of the Ca^{2+} ion is in the form of a capped trigonal antiprism which consists of the tetradentate NTA ligand and three nonchelated oxygen atoms from symmetry-related ligands. The sodium ions, which serve to balance the charge, bridge the Ca^{2+} trigonal coordination planes. The Na^+ ion is in a trigonal-antiprismatic coordination environment of six oxygen atoms from six symmetry-related NTA ligands. Each of the exocyclic oxygen atoms of the NTA ligand link the complexes to three other CaNTA complexes. The NTA ligand has threefold symmetry crystallographically imposed. Its geometry is not remarkably different from that observed in Na_3NTA.[19] Bond distances and angles are not unusual. Details of the cation coordination

Table VI

Coordination Geometries of $CaEDTA^{2-}$ and $CaNTA^-$ Glycinate Rings[a]

	G_1 eq	G_2 ax	G_3 ax	G_4 eq	average (rms)	G_5	Lee[15]
			Distances (Å)				
C-N	1.453 (13)	1.482 (12)	1.483 (12)	1.466 (13)	1.471 (14)	1.475	1.48 (1)
C-C′	1.523 (13)	1.529 (15)	1.522 (14)	1.535 (13)	1.527 (6)	1.524	1.52 (1)
C-O	1.260 (12)	1.265 (12)	1.263 (12)	1.269 (12)	1.264 (4)	1.254	1.27 (2)
C-O′	1.245 (13)	1.237 (12)	1.257 (11)	1.235 (13)	1.244 (10)	1.250	
Ca-O	2.378 (7)	2.370 (7)	2.414 (7)	2.473 (7)	2.408 (47)	2.365	
			Angles (deg)				
N-C-C′	110.6 (8)	114.3 (8)	113.9 (8)	113.8 (8)	113.2 (1.7)	111.7	111 (2)
C-C′-O	117.7 (9)		117.3 (8)	118.6 (8)	117.9 (.4)	116.8	118 (2)
C-C′-O′	120.3 (9)	117.0 (9)	117.5 (9)	115.1 (8)	117.5 (1.9)	117.6	
O-C′-O′	122.1 (9)	125.1 (10)	125.0 (9)	126.2 (9)	124.6 (1.8)	125.6	
Ca-N-C	107.7 (6)	106.8 (6)	103.1 (5)	109.3 (5)	106.7 (2.6)	107.4	107 (2)
Ca-O-C′	126.9 (6)	126.4 (6)	121.0 (6)	122.1 (6)	124.1 (3.0)		
O-Ca-N	64.3 (2)	66.9 (2)	68.4 (2)	66.4 (2)	66.7 (1.0)		
			Torsion Angles (deg)				
CaNCC′	38.2	29.4	43.4	34.0		−37.5	
NCC′O	−32.8	−29.7	−39.0	−24.4		26.2	
CC′OCa	6.1	11.4	8.4	0.9		3.5	
C′OCaN	11.5	4.0	11.8	14.3		−18.3	
OCaNC	−26.3	−17.7	−28.0	−24.6		28.2	

Ethylenediamine Ring Geometry of $CaEDTA^{2-}$

	distances, Å		angles, deg		torsion angles, deg
C1-N1	1.482 (12)	N1-Ca-N2	67.2 (2)	Ca-N1-C1-C2	−45.1
C1-C2	1.509 (15)	Ca-N1-C1	110.4 (5)	N1-C1-C2-N2	57.9
C2-N2	1.483 (12)	N1-C1-C2	110.8 (8)	C1-C2-N2-Ca	−38.7
Ca-N1	2.711 (8)	C1-C2-N2	113.9 (8)	C2-N2-Ca-N1	10.0
Ca-N2	2.623 (7)	C2-N2-Ca	113.4 (5)	N2-Ca-N1-C1	18.6
N1-C3	1.453 (13)	C1-N1-C3	111.7 (7)		
N1-C5	1.482 (12)	C1-N1-C5	110.3 (7)		
N2-C7	1.483 (12)	C3-N1-C5	109.8 (7)		
N2-C9	1.466 (13)	C2-N2-C7	111.1 (7)		
		C2-N2-C9	109.8 (7)		
		C7-N2-C9	109.9 (7)		

[a] The numbering of the glycinate rings G_1–G_4 is seen in Figure 1. G_1 begins with C3, G_2 begins with C5, G_3 begins with C9, and G_4 begins with C7. G_5 is the glycinate ring in Na(CaNTA) in Figure 3.

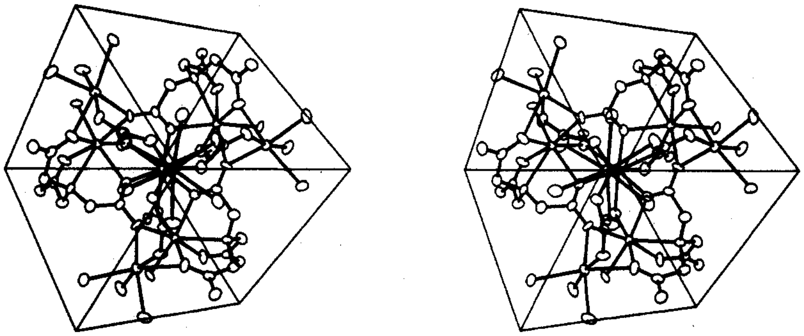

Figure 2. Unit cell packing diagram for Na(CaNTA). Hydrogen atoms are not included for clarity. Open bonds represent coordination bonds and solid bonds represent covalent bonds.

are included in Tables V and VI.

Discussion

The structural analyses reported here confirm for the first time the structures of the most widely studied complexes of Ca^{2+}, $CaEDTA^{2-}$, and $CaNTA^-$. It has been often predicted, most significantly by Hoard and co-workers, that on the basis of the Ca^{2+} size/charge ratio these complexes should have coordination numbers greater than 6. This has now been borne out in these studies of the crystals $Ca(CaEDTA)\cdot 7H_2O$ and Na(CaNTA) both of which were obtained from highly aqueous environments. The results show that in these crystals $CaEDTA^{2-}$ and $CaNTA^-$ exhibit eightfold and sevenfold coordinations, respectively. Furthermore, there is no reason to believe that such is not the case in the more dilute environment of an aqueous solution where the nonchelated coordination sites would be occupied by water molecules. While examples of coordination numbers even greater would not be unexpected, a recent review[8] of 70 calcium coordination environments in amino acid related complexes points to a pronounced preference for eightfold coordination in 29 cases and sevenfold coordination in 21 cases. Only six complexes demonstrated ninefold coordination; interestingly, no multidentate (i.e., bidentate or greater) complexes were observed among the 14 examples of sixfold coordination complexes.

The maximum symmetry available to the Na(CaNTA) salt in the space group is utilized. The crystallographic threefold axis passes through the nitrogen of the NTA ligand and both

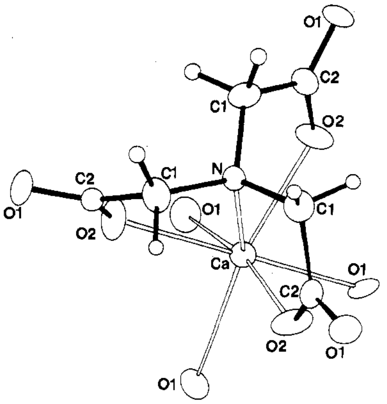

Figure 3. Coordination and ligand geometry for CaNTA$^-$. Sodium atoms are not included for clarity.

cations. The three (2_1) screw axes stagger the oxygen atoms into idealized antiprismatic coordinations about both cations. While the NTA could potentially have $3m$ (C_{3v}) symmetry, the size of the Ca^{2+} ion and the torsional angles in the glycinate rings suggest the threefold symmetry to be the highest practical symmetry for this ligand.

In contrast to the compact crystal structure of Na(CaNTA), Ca(CaEDTA)$\cdot 7H_2O$ has an open structure with a complex hydrogen-bond network. Four of the seven water molecules are not coordinated to calcium ions and the crystals lose crystallinity upon standing for prolonged periods of time. The presence of four noncoordinated water molecules coexisting with the eight- and seven-coordinate calcium ions suggests that these coordination numbers represent saturation for these complexes.

Only one eight-coordinate EDTA complex has been reported, ZrEDTA$\cdot 4H_2O$.[20] This complex has a tendency toward square-antiprismatic coordination, although the coordination has been described as a dodecahedral configuration at the given state of refinement. It has previously been implied by Hoard and others that ideal coordination geometries in multidentate EDTA complexes are not possible unless equivalent bond lengths between the metal and nitrogen and oxygen coordinating sites can be achieved.[21] For EDTA complexes of predominately electrostatic binding metal ions, such as Ca^{2+} and Zr^{4+}, this idealized geometry should not be expected since the interactions between such metals and amine nitrogens are relatively weak. In fact, the M–N bond lengths in both the Ca^{2+} and Zr^{4+} complexes are all significantly longer than the corresponding M–O bond lengths. This has also found for two seven-coordinate $H_2O\cdot MgEDTA^{2-}$ structures.[21,22]

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Registry No. Ca(CaEDTA)$\cdot 7H_2O$, 29990-17-8; Na(CaNTA), 60034-45-9.

Supplementary Material Available: Listings of anisotropic thermal parameters (Tables A-I, A-II) and structure factor amplitudes (Tables A-III, A-IV) (19 pages). Ordering information is given on any current masthead page.

References and Notes

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