CRYSTAL STRUCTURES OF ETHYLENEDIAMINOTETRAACETATO CALCIUM AND SODIUM COMPLEXES

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Introduction

Calcium Hydrogen Complex: A solution of 2.05 g. ethylenediaminotetraacetatic acid and 0.68 g. calcium carbonate was adjusted to pH 3.3 with HCl. After the solution was filtered, it was allowed to evaporate at ambient conditions. Colourless, irregularly shaped parallelepiped crystals were obtained.

Dicalcium Complex: A solution of 2 g. H_4EDTA and 1.37 g. $CaCO_3$, was adjusted to pH 8. After the solution was filtered, it was allowed to evaporate at ambient conditions. Colourless, irregularly shaped parallelepiped crystals were obtained.

We made the synthesis with a solution of the calcium salt, then we decreased the pH with HCl, and arrived at the same result. At pH 8-4 we obtained dicalcium salt and 3-4 calcium hydrogen salts.

Disodium Complex: A solution of 2.0 g. H_4EDTA and 0.73 g. Na_2CO_3 was adjusted to pH 5 with HCl. After the solution was filtered, it was allowed to evaporate at ambient conditions. Colourless, irregulary shaped parallelepiped crystals were obtained.

Tetrasodium Complex: A solution of 2 g. H_4EDTA and 1.37 g. Na_2CO_3 was adjusted to pH 10. After the solution was filtered, it was allowed to evaporate at ambient conditions. Colourless, irregularly shaped parallelepiped crystals were obtained.

Description of the structures

Crystal data. $C_{10}H_{14}N_2O_8Ca(H_2O)_2$. Fw = 393, monoclinic, **a** = 15.998(4); **b** = 18.362(2); **c** = 5.426(2); β = 90.51(2). V = 1593.9(1)Å^3,

$P2_1/n$, Dx = 1.64 g cm^{-3}, Z = 4, F(000) = 848.0, (Mo Kα) = 0.71069 Å, (Mo Kα) = 4.56 cm^{-1}. 298 K

Experimental. A prismatic crystal (0.1x0.1x0.2 mm) was selected and mounted on a Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 \leq \theta \leq 12$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using scan technique. 2193 reflections were measured in the range $2 \leq \theta \leq 25$. 1186 reflections were assumed as observed applying the condition $I \geq 2.5\ \sigma(I)$. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization but no absorption corrections were made.

Table 1. Positional parametres and anisotropic thermal parameters of the nonhydrogen atoms (X10000) of $(C_{10}H_{14}N_2O_8Ca(H_2O)_2)\ 1.5H_2O$.
The temperature factor is of the form $\exp(-2\pi\ u_{IJ}\ h_I\ h_J\ a_I^*\ a_J^*)$.
($BEQ = 8\ \pi^2/3\ u_{IJ}\ a_I^*\ a_J^*\ a_I.a_J$)

	X/A	Y/B	Z/C	BEQ	U11	U22	U33	U23	U13	U12
CA	2541(1)	416(1)	7632(4)	2.44(8)	353(10)	230(9)	346(11)	69(11)	86(9)	-5(11)
N(1)	4134(4)	2080(4)	2730(12)	1.46(29)	232(38)	133(35)	190(39)	-40(35)	26(31)	-88(35)
C(1)	4705(5)	2163(4)	594(15)	1.80(40)	288(51)	246(54)	150(46)	-20(43)	59(41)	10(47)
C(2)	5194(5)	2886(4)	573(15)	1.56(37)	190(48)	236(49)	165(44)	31(44)	-4(37)	-55(42)
N(2)	5821(4)	2965(3)	2629(11)	1.18(28)	185(36)	118(35)	147(36)	-15(35)	35(30)	36(33)
O(11)	3061(4)	3640(4)	5245(13)	3.95(38)	352(42)	453(48)	697(55)	-207(42)	49(39)	171(37)
O(12)	4365(4)	3250(3)	5578(10)	2.34(31)	329(42)	315(39)	243(36)	-63(31)	-11(31)	33(32)
C(11)	3631(6)	3229(5)	4694(16)	1.72(43)	319(59)	103(51)	232(53)	-18(42)	61(47)	56(44)
C(12)	3423(5)	2654(4)	2766(16)	1.76(40)	259(54)	101(42)	309(55)	1(42)	32(43)	28(38)
O(21)	3247(5)	470(4)	5497(14)	4.70(42)	746(57)	267(45)	780(57)	127(45)	330(47)	-86(43)
O(22)	3313(4)	1624(4)	6793(11)	3.12(34)	480(46)	471(47)	235(37)	-24(37)	25(33)	-125(38)
C(21)	3408(5)	1134(6)	5281(18)	2.25(51)	168(55)	230(67)	457(73)	153(54)	-30(50)	-7(49)
C(22)	3794(5)	1313(4)	2772(15)	1.65(41)	177(51)	133(48)	319(57)	-7(43)	79(43)	-60(38)
O(31)	6884(4)	4562(4)	5109(11)	2.99(33)	524(45)	255(39)	357(42)	-69(35)	-25(35)	-195(39)
O(32)	6608(4)	3465(3)	6700(11)	2.74(32)	422(44)	408(41)	212(35)	75(36)	10(32)	-94(34)
C(31)	6603(5)	3911(6)	5018(16)	1.95(47)	268(60)	307(66)	166(53)	-61(48)	88(45)	-2(52)
C(32)	6189(5)	3717(4)	2531(15)	1.98(41)	268(55)	168(47)	315(55)	-21(46)	-86(44)	-29(41)
O(41)	6771(4)	1286(4)	4719(11)	3.31(36)	527(49)	364(43)	367(43)	87(36)	112(36)	300(37)
O(42)	5583(4)	1844(3)	5664(11)	2.24(30)	286(39)	218(35)	347(39)	74(30)	120(32)	96(28)
C(41)	6245(6)	1794(5)	4506(16)	1.87(43)	240(57)	222(55)	246(53)	-89(44)	-65(45)	115(44)
C(42)	6481(5)	2386(4)	2632(16)	1.93(40)	210(52)	191(46)	335(55)	2(45)	111(44)	98(40)
OW(1)	1539(4)	-311(4)	4393(12)	3.49(34)	506(44)	446(45)	375(41)	-24(37)	-3(34)	75(37)
OW(2)	3552(5)	-537(4)	10790(17)	7.76(58)	1195(82)	691(63)	1051(74)	249(58)	-608(65)	-189(55)
OW(3)	4880(4)	4570(3)	-2681(13)	4.18(37)	516(45)	426(42)	647(52)	-119(45)	134(39)	119(41)

The structure was solved by direct methods, using SHELX76 computer program and refined by full-matrix least-squares method, with the

SHELX76 computer program. The function minimized was Σ w | |Fo| - |Fc|^2, where w = (σ^2(Fo) + 0.0087 | Fo |^2)$^{-1}$. f, f' and f'' were taken from International Tables for X-ray Crystallography. Two hydrogen atoms of the amine group were located from a difference synthesis and the remaining hydrogen atoms were computed. The refinement was made with an overall isotropic temperature factor, using a gliding model for the computed atoms. The final R factor was 0.054 (wR = 0.054) for all observed reflections. A total of 226 parameters were refined. Max. shift/e.s.d. = 0.1, Max. and min. peaks in final difference synthesis were 0.3 and −0.4 eÅ^{-3}, respectively.

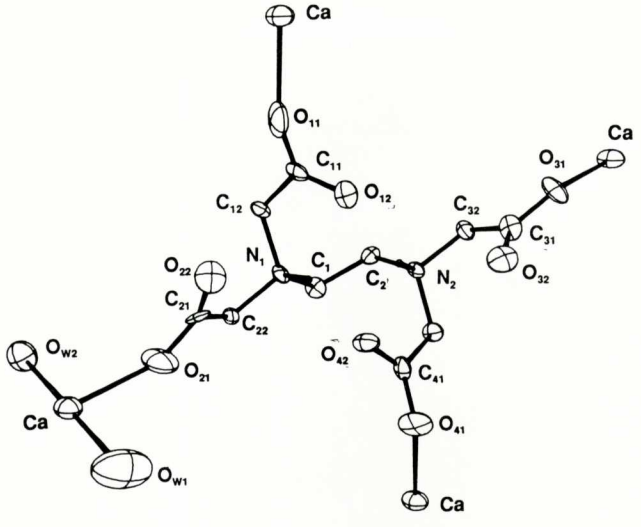

Figure 1. A stereoscopic view of the molecule $C_{10}H_{14}N_2O_8Ca(H_2O)_2$

Table 2. Bond distances and angles in $C_{10}H_{14}N_2O_8Ca(H_2O)_2$

Bond distances (Å)					
C(1)	---N(1)	1.490(9)	C(21)	---O(21)	1.252(10)
C(12)	---N(1)	1.551(9)	C(21)	---O(22)	1.227(11)
C(22)	---N(1)	1.510(9)	C(22)	---C(21)	1.535(11)
C(2)	---C(1)	1.540(10)	C(31)	---O(31)	1.279(10)
N(2)	---C(2)	1.501(9)	C(31)	---O(32)	1.225(10)
C(32)	---N(2)	1.502(9)	C(32)	---C(31)	1.539(11)
C(42)	---N(2)	1.499(9)	C(41)	---O(41)	1.260(10)
C(11)	---O(12)	1.222(10)	C(41)	---O(42)	1.239(9)
C(11)	---O(11)	1.266(10)	C(42)	---C(41)	1.538(11)
C(12)	---C(11)	1.521(11)			

Bonds angles (º)							
C(12)	-N(1)	-C(1)	113.2(6)	O(22)	-C(21)	-O(21)	128.6(9)
C(22)	-N(1)	-C(1)	109.4(6)	C(22)	-C(21)	-O(21)	112.1(9)
C(22)	-N(1)	-C(12)	111.7(6)	C(22)	-C(21)	-O(22)	119.3(8)
C(2)	-C(1)	-N(1)	114.2(7)	C(21)	-C(22)	-N(1)	111.1(7)
N(2)	-C(2)	-C(1)	114.5(7)	O(32)	-C(31)	-O(31)	126.5(9)
C(32)	-N(2)	-C(2)	108.8(6)	C(32)	-C(31)	-O(31)	113.5(8)
C(42)	-N(2)	-C(2)	113.5(6)	C(32)	-C(31)	-O(32)	119.9(8)
C(42)	-N(2)	-C(32)	112.0(6)	C(31)	-C(32)	-N(2)	110.3(7)
O(11)	-C(11)	-O(12)	125.5(9)	O(42)	-C(41)	-O(41)	125.5(9)
C(12)	-C(11)	-O(12)	116.0(9)	C(42)	-C(41)	-O(41)	114.5(8)
C(12)	-C(11)	-O(11)	118.5(8)	C(42)	-C(41)	-O(42)	119.9(7)
C(11)	-C(12)	-N(1)	109.0(7)	C(41)	-C(42)	-N(2)	108.9(7)
C(21)	-O(21)	-CA	147.0(7)				

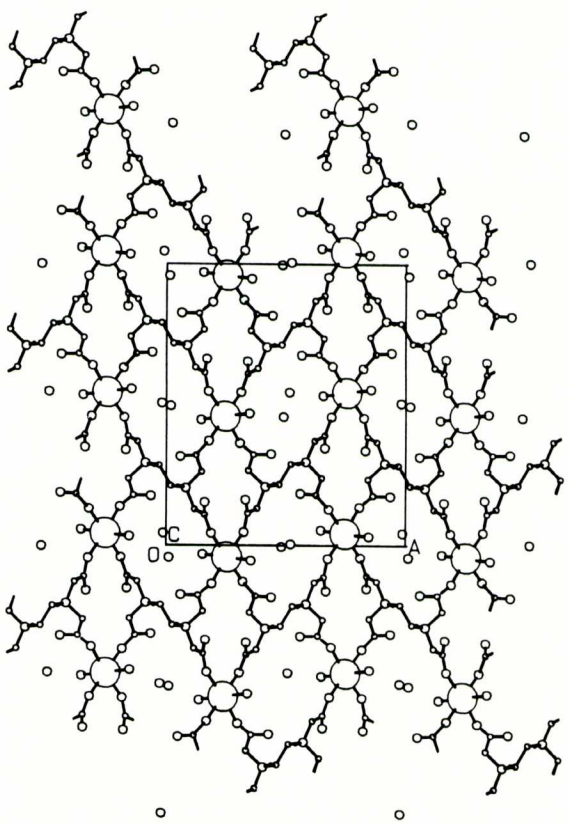

Figure 2. Projection along the b axis showing the packing scheme.

Crystal data. $C_{10}H_{14}N_2O_8Ca(H_2O)$. Fw = 366, orthorrhombic, **a** = 18.916(5); **b** = 17.881(5); **c** = 8.572(3). V = 2899.4(1)Å^3, Pcab, Dx = 1.68 g cm^{-3}, Z = 8, F(000) = 15360, (Mo K$^{\alpha}$) = 0.71069 Å, (Mo Kα = 4.81 cm^{-1}. 298 K

Experimental. A prismatic crystal (0.1x0.1x02 mm) was selected and mounted on a Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 \leq \theta \leq 12$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using scan technique. 2744 reflections were measured in the range $2 \leq \theta \leq 25$. 1853 reflections were assumed as observed applying the condition $I \geq 2.5\ \sigma(I)$. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization but no absorption corrections were made.

Table 3. Positional parameters and anisotropic thermal parameters of the nonhydrogen atoms (X10000) of $[(C_{10}H_{14}N_2O_8Ca(H_2O)]H_2O$.
The temperature factor is of the form $\exp(-2\pi\ u_{IJ}\ h_I\ h_J\ a_I^*\ a_J^*)$.
($BEQ = 8\ \pi^2/3\ u_{IJ}\ a_I^*\ a_J^*\ a_I.a_J$)

	X/A	Y/B	Z/C	BEQ	U11	U22	U33	U23	U13	U12
CA	2541(1)	-416(1)	7632(4)	2.44(8)	279(6)	365(6)	173(6)	12(4)	-6(4)	-26(4)
N (1)	4134(4)	2080(4)	2730(12)	1.46(29)	269(23)	305(22)	86(22)	-16(17)	65(17)	-23(18)
C (1)	4705(5)	2163(4)	594(15)	1.80(40)	368(30)	340(29)	78(24)	-57(22)	13(22)	-48(23)
C (2)	5194(5)	2886(4)	573(15)	1.56(37)	314(28)	346(29)	92(24)	45(21)	-43(21)	-33(22)
N (2)	5821(4)	2965(3)	2629(11)	1.18(28)	227(22)	302(22)	84(20)	15(17)	-17(15)	0(18)
O(11)	3061(4)	3640(4)	5245(13)	3.95(38)	257(20)	606(26)	214(21)	52(19)	-26(16)	56(18)
O(12)	4365(4)	3250(3)	5578(10)	2.34(31)	289(19)	521(25)	154(18)	54(18)	49(15)	85(18)
C(11)	3631(6)	3229(5)	4694(16)	1.72(43)	219(25)	417(31)	110(24)	-42(24)	8(21)	7(23)
C(12)	3423(5)	2654(4)	2766(16)	1.76(40)	240(26)	332(29)	228(28)	6(23)	17(23)	38(23)
O(21)	3247(5)	470(4)	5497(14)	4.70(42)	466(25)	459(23)	239(22)	-76(18)	121(18)	-183(20)
O(22)	3313(4)	1624(4)	6793(11)	3.12(34)	290(19)	469(23)	117(18)	-84(16)	73(15)	-50(16)
C(21)	3408(5)	1134(6)	5281(18)	2.25(51)	223(26)	307(29)	169(25)	-43(22)	-4(21)	9(21)
C(22)	3794(5)	1313(4)	2772(15)	1.65(41)	310(28)	364(29)	140(25)	-12(23)	65(22)	-143(24)
O(31)	6884(4)	4562(4)	5109(11)	2.99(33)	409(23)	454(24)	178(19)	57(18)	-108(18)	12(17)
O(32)	6608(4)	3465(3)	6700(11)	2.74(32)	610(28)	579(28)	361(27)	223(21)	-98(23)	-228(24)
C(31)	6603(5)	3911(6)	5018(16)	1.95(47)	272(26)	369(30)	139(25)	54(23)	-3(22)	-5(24)
C(32)	6189(5)	3717(4)	2531(15)	1.98(41)	287(28)	329(28)	175(25)	53(22)	-10(22)	-74(23)
O(41)	6771(4)	1286(4)	4719(11)	3.31(36)	231(19)	444(23)	267(22)	-8(18)	-2(15)	42(17)
O(42)	5583(4)	1844(3)	5664(11)	2.24(30)	270(20)	408(23)	354(23)	-116(19)	-111(17)	76(16)
C(41)	6245(6)	1794(5)	4506(16)	1.87(43)	306(29)	365(31)	135(27)	25(23)	-2(21)	37(23)
C(42)	6481(5)	2386(4)	2632(16)	1.93(40)	192(25)	393(30)	245(27)	-26(24)	18(22)	30(23)
OW(1)	1539(4)	-311(4)	4393(12)	3.49(34)	800(40)	378(27)	813(40)	-126(30)	486(32)	-46(28)
OW(2)	3552(5)	-537(4)	10790(17)	7.76(58)	884(39)	768(36)	307(26)	-159(25)	218(24)	-401(31)
OW(3)	4880(4)	4570(3)	-2681(13)	4.18(37)						
OW(4)	5193(13)	45(11)	1717(38)	3.27(16)						
OW(4)"	4844(18)	-291(15)	3312(56)	3.89(26)						

Table 4. Bond distances and angles in $C_{10}H_{14}N_2O_8Ca(H_2O)$

Bond distances (Å)

C(1)	---N(1)	1.528(6)	C(21)	---O(21)	1.247(6)
C(12)	---N(1)	1.514(6)	C(21)	---O(22)	1.279 (6)
C(22)	---N(1)	1.466(6)	C(22)	---C(21)	1.583 (7)
C(2)	---C(1)	1.474(6)	C(31)	---O(31)	1.256 (6)
N(2)	---C(2)	1.497(6)	C(31)	---O(32)	1.228 (6)
C(32)	---N(2)	1.550(6)	C(32)	---C(31)	1.501 (7)
C(42)	---N(2)	1.482(6)	C(41)	---O(41)	1.252 (6)
C(11)	---O(11)	1.239(6)	C(41)	---O(42)	1.230 (6)
C(11)	---O(12)	1.252(6)	C(42)	---C(41)	1.503 (7)
C(12)	---C(11)	1.570(7)			

Bond angles (°)

C(12)	-N(1)	-C(1)	112.3(3)	C(22)	-C(21)	-O(21)	115.5(3)
C(22)	-N(1)	-C(1)	106.2(2)	C(22)	-C(21)	-O(21)	115.5(3)
C(22)	-N(1)	-C(12)	111.9(3)	C(22)	-C(21)	-O(21)	115.5(3)
C(2)	-C(1)	-N(1)	116.5(3)	C(22)	-C(21)	-O(21)	115.5(3)
N(2)	-C(2)	-C(1)	110.6(3)	C(22)	-C(21)	-O(21)	115.5(3)
C(32)	-N(2)	-C(2)	107.8(2)	C(22)	-C(21)	-O(21)	115.5(3)
C(42)	-N(2)	-C(2)	113.8(2)	C(22)	-C(21)	-O(22)	120.5(7)
C(42)	-N(2)	-C(32)	113.9(2)	C(21)	-C(22)	-N(1)	114.2(3)
O(12)	-C(11)	-O(11)	131.7(6)	O(32)	-C(31)	-O(31)	122.7(7)
C(12)	-C(11)	-O(11)	111.1(6)	C(32)	-C(31)	-O(31)	121.3(7)
C(12)	-C(11)	-O(12)	117.2(3)	C(32)	-C(31)	-O(32)	115.8(3)
C(11)	-C(12)	-N(1)	110.6(2)	C(31)	-C(32)	-N(2)	109.2(3)
O(22)	-C(21)	-O(21)	124.0(7)	C(41)	-O(41)	-CA	143.2(2)
C(22)	-C(21)	-O(21)	115.5(3)	O(42)	-C(41)	-O(41)	127.0(3)
C(22)	-C(21)	-O(21)	115.5(3)	C(42)	-C(41)	-O(41)	116.1(3)
C(22)	-C(21)	-O(21)	115.5(3)	C(42)	-C(41)	-O(42)	116.8(3)
C(22)	-C(21)	-O(21)	115.5(3)	C(41)	-C(42)	-N(2)	113.4(3)

The structure was solved by direct methods, using MULTAN computer program and refined by full-matrix least-squares method, with the SHELX76 computer program. The function minimized was Σ w $| |Fo| - |Fc|^2$, where $w = (\sigma^2(Fo) + 0.0005 | Fo |^2)^{-1}$. f, f' and f'' were taken from International Tables for X-ray Crystallography. All hydrogen atoms were calculated with a computer program. All atomic coordinates were refined with an overall isotropic temperature factor, using a gliding model for computed atoms. The final R factor was 0.077 (wR = 0.081) for all observed reflections. A total of 215 parameters were refined. Max. shift/e.s.d = 0.1, Max. and min. peaks in final difference synthesis was 0.3 and -0.3 $eÅ^{-3}$, respectively.

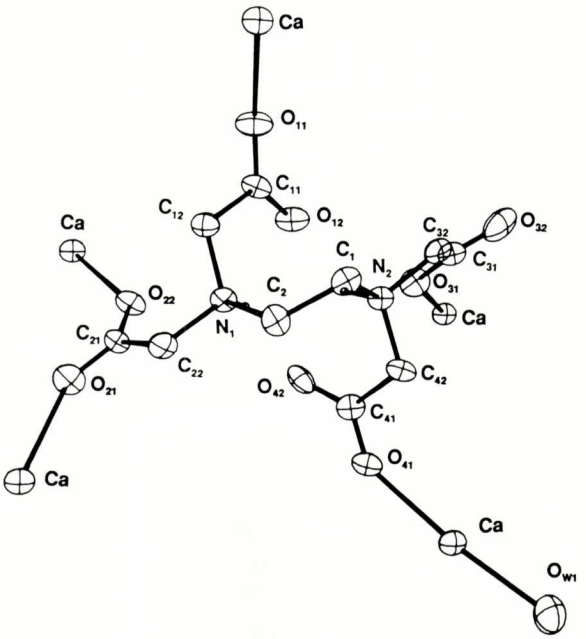

Figure 3. A stereoscopic view of the molecule $C_{10}H_{14}N_2O_8Ca(H_2O)$

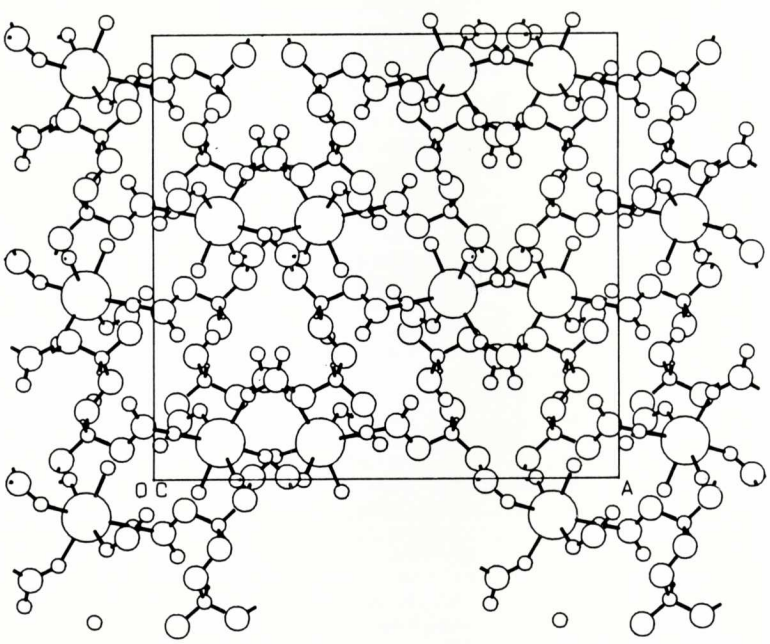

Figure 4. Projection along the b axis showing the packing scheme.

Crystal data. $[C_{10}H_{12}N_2O_8Ca(H_2O)Ca(H_2O)_2]2.75(H_2O)$. Fw = 499, triclinic, **a** = 11.233(53; **b** = 10.123(2); **c** = 9.894(2). α = 106.22(2); β = 102.96(2); τ = 103.42(2) V = 999.2(8)Å^3, P-1, Dx = 1.49 g cm^{-3}, Z = 2, F(000) = 500, (Mo Kα) = 0.71069Å, (Mo Kα) = 6.21 cm^{-1}. 298 K

Experimental. A prismatic crystal (0.1x0.1x0.2 mm) was selected and mounted on a Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 \leq \theta \leq 12$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using scan technique. 3417 reflections were measured in the range $2 \leq \theta \leq 25$. 2537 reflections were assumed as observed applying the condition $I \geq 2.5\ \sigma(I)$. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization but no absorption corrections were made.

Table 5. Positional parameters and anisotropic thermal parameters of the nonhydrogen atoms (X10000) of $[(C_{10}H_{12}N_2O_8Ca(H_2O))Ca(H_2O)_2]$ 2.75H_2O. The temperature factor is of the form $\exp(-2\pi\ u_{IJ}\ h_I\ h_J\ a_I^*\ a_J^*)$. ($BEQ = 8\ \pi^2/3\ u_{IJ}\ a_I^*\ a_J^*\ a_I.a_J$)

	X/A	Y/B	Z/C	BEQ	U11	U22	U33	U23	U13	U12
CA(1)	3404(1)	-1505(1)	3509(1)	1.97(4)	232(4)	232(5)	236(5)	82(3)	51(3)	6(3)
CA(2)	1877(1)	-3864(1)	6233(1)	2.17(4)	250(5)	245(5)	270(5)	92(4)	57(3)	-11(4)
N (1)	868(3)	-2020(4)	2118(4)	1.77(14)	222(18)	181(18)	213(17)	65(14)	58(14)	-26(14)
C (1)	689(4)	-1854(5)	662(5)	2.02(17)	200(21)	274(24)	219(21)	97(18)	4(17)	-16(18)
C (2)	1659(4)	-499(5)	769(5)	2.04(18)	218(21)	259(24)	277(24)	143(19)	37(18)	13(18)
N (2)	3022(3)	-452(4)	1380(4)	1.72(14)	173(17)	172(18)	224(18)	64(14)	-1(14)	-32(14)
O(11)	2639(3)	451(3)	4444(3)	2.40(13)	211(16)	267(17)	329(17)	11(14)	44(13)	37(13)
C(11)	1476(4)	444(5)	4025(5)	2.10(18)	231(22)	274(24)	259(23)	65(18)	71(18)	54(18)
O(12)	1117(3)	1535(4)	4393(4)	3.44(16)	328(18)	279(19)	592(24)	29(17)	86(17)	102(15)
C(12)	449(4)	-980(5)	3096(6)	2.39(19)	185(21)	305(25)	380(27)	85(21)	106(19)	26(19)
O(21)	1948(3)	-3241(4)	4020(3)	2.48(13)	234(16)	359(19)	266(16)	161(14)	9(13)	-60(14)
C(21)	750(4)	-3811(5)	3334(5)	2.11(18)	237(22)	239(23)	219(22)	75(18)	39(18)	-88(19)
O(22)	49(3)	-4617(4)	3763(4)	2.82(14)	279(16)	391(19)	296(17)	170(15)	38(14)	-105(15)
C(22)	192(5)	-3490(5)	1964(5)	2.29(18)	285(24)	223(23)	232(23)	63(19)	13(19)	-74(19)
O(31)	5265(3)	498(3)	3779(3)	1.97(12)	208(15)	239(16)	236(15)	95(13)	23(12)	-18(13)
C(31)	5159(4)	1318(5)	3038(5)	1.87(17)	230(21)	195(21)	216(22)	54(17)	52(17)	-21(18)
O(32)	6031(3)	2391(4)	3182(4)	3.27(16)	277(18)	365(20)	440(21)	197(17)	-14(15)	-145(15)
C(32)	3872(4)	1050(5)	1921(5)	1.95(17)	270(22)	154(21)	249(23)	73(18)	57(18)	-42(17)
O(41)	2933(3)	-3306(3)	1100(3)	2.49(14)	462(19)	246(17)	210(16)	85(13)	86(14)	71(14)
C(41)	2946(4)	-2966(5)	-21(5)	1.77(17)	184(19)	250(22)	199(22)	64(18)	27(16)	48(17)
O(42)	2654(3)	-3835(3)	-1305(3)	2.54(13)	369(18)	280(17)	204(16)	44(132)	20(13)	14(14)
C(42)	3422(5)	-1364(5)	243(5)	1.90(18)	241(22)	283(24)	173(21)	95(18)	56(18)	22(19)
OW(1)	5144(4)	-2619(4)	3739(5)	3.24(17)	332(19)	297(21)	439(23)	-5(17)	7(19)	79(16)
OW(2)	2593(25)	-5622(21)	5061(31)	5.60(74)	735(86)	1(55)	1378(140)	208(83)	417(83)	41(60)
OW(2)'	2587(26)	-5941(27)	5290(36)	4.75(89)	523(80)	198(104)	1319(154)	349(79)	541(96)	187(66)
OW(3)	1166(4)	-1831(4)	6883(5)	3.40(18)	398(23)	296(21)	466(23)	62(19)	14(18)	77(17)
OW(4)	3058(5)	782(5)	7856(6)	4.78(23)	618(28)	532(27)	738(32)	300(26)	306(25)	120(24)
OW(5)	3742(10)	3808(10)	8714(11)	4.88(47)	868(72)	552(51)	595(55)	225(46)	219(53)	500(47)
OW(6)	2520(14)	-5881(12)	1810(16)	2.71(59)	607(92)	12(51)	471(80)	106(52)	327(74)	20(55)
OW(6)'	2755(18)	-6102(20)	935(22)	4.62(12)	658(61)	489(56)	1934(122)	559(67)	862(74)	234(48)
OW(7)	4402(9)	-5450(10)	3838(15)	7.13(63)	585(45)					
OW(7)'	4937(24)	-5449(28)	1636(27)	7.20(18)	911(69)					

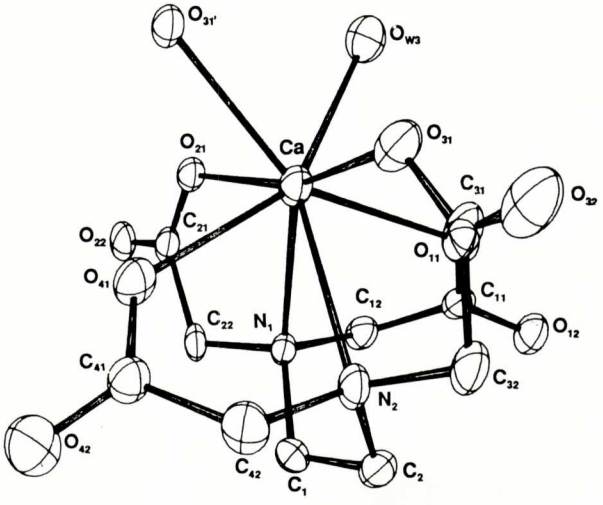

Figure 5. A stereoscopic view of the molecule $[(C_{10}H_{12}N_2O_8Ca(H_2O)Ca(H_2O)_2]2.75(H_2O)$

The structure was solved by direct methods, using SHELX76 computer program and refined by full-matrix least-squares method, with the SHELX76 computer program. The function minimized was Σ w | |Fo| - |Fc|^2, where w = $(\sigma^2(Fo) + 0.0048 \mid Fo \mid^2)^{-1}$. f, f' and f'' were taken from International Tables for X-ray Crystallography. All hydrogen atoms were located from a difference synthesis. All atomic coordinates were refined with an overall isotropic temperature factor, using a gliding model for computed atoms. The final R factor was 0.049 (wR = 0.056) for all observed reflections. Number of refined parameters was 337. Max. shift/e.s.d = 0.1, Max. and min. peaks in final difference synthesis were 0.3 and -0.3 eÅ^{-3}, respectively.

Table 6. Bond distances and angles in $[(C_{10}H_{12}N_2O_8Ca(H_2O)Ca(H_2O)_2]2.75(H_2O)$

Bond distances (Å)					
C(1)	---N(1)	1.470(5)	C(21)	---O(21)	1.271(5)
C(12)	---N(1)	1.460(6)	O(22)	---C(21)	1.236(5)
C(22)	---N(1)	1.458(5)	C(22)	---C(21)	1.510(6)
C(2)	---C(1)	1.508(6)	C(31)	---O(31)	1.258(5)
N(2)	---C(2)	1.495(5)	O(32)	---C(31)	1.238(5)
C(32)	---N(2)	1.471(5)	C(32)	---C(31)	1.516(6)
C(42)	---N(2)	1.469(6)	C(41)	---O(41)	1.251(5)
C(11)	---O(11)	1.273(5)	O(42)	---C(41)	1.244(5)
O(12)	---C(11)	1.248(6)	C(42)	---C(41)	1.515(6)
C(12)	---C(11)	1.508(6)			

Bond angles (°)							
C(1)	-N(1)	-CA(1)	110.3(1)	C(21)	-O(21)	-CA(1)	126.2(1)
C(12)	-N(1)	-CA(1)	106.3(1)	C(21)	-O(21)	-CA(2)	95.7(1)
C(12)	-N(1)	-C(1)	111.6(1)	O(22)	-C(21)	-O(21)	121.4(1)
C(22)	-N(1)	-CA(1)	107.2(1)	C(22)	-C(21)	-O(21)	118.5(1)
C(22)	-N(1)	-C(1)	111.0(1)	C(22)	-C(21)	-O(22)	120.2(1)
C(22)	-N(1)	-C(12)	110.1(1)	C(21)	-O(22)	-CA(2)	90.3(1)
C(2)	-C(1)	-N(1)	111.1(1)	C(21)	-C(22)	-N(1)	110.3(1)
N(2)	-C(2)	-C(1)	113.3(1)	C(31)	-O(31)	-CA(1)	121.4(1)
C(2)	-N(2)	-CA(1)	114.0(1)	O(32)	-C(31)	-O(31)	124.7(1)
C(32)	-N(2)	-CA(1)	109.1(1)	C(32)	-C(31)	-O(31)	119.6(1)
C(32)	-N(2)	-C(2)	109.6(1)	C(32)	-C(31)	-O(32)	115.6(1)
C(42)	-N(2)	-CA(1)	103.5(1)	C(31)	-C(32)	-N(2)	113.8(1)
C(42)	-N(2)	-C(2)	110.9(1)	C(41)	-O(41)	-CA(1)	121.7(1)
C(42)	-N(2)	-C(32)	109.6(1)	C(41)	-C(42)	-CA(2)	137.5(1)
C(11)	-O(11)	-C(A1)	125.1(1)	C(41)	-C(42)	-N(2)	114.3(1)
O(12)	-C(11)	-O(11)	124.1(1)	O(42)	-C(41)	-O(41)	125.3(1)
C(12)	-C(11)	-O(11)	118.4(1)	C(42)	-C(41)	-O(41)	116.4(1)
C(12)	-C(11)	-O(12)	117.3(1)	C(42)	-C(41)	-O(42)	118.2(1)
C(11)	-C(12)	-N(1))	114.9(1)	O(W2)'	-O(W2)	-CA(2)	109.0(7)
CA(2)	-O(21)	-CA(1)	134.7(1)	O(W2)	-O(W2)'	-CA(2)	61.1(7)

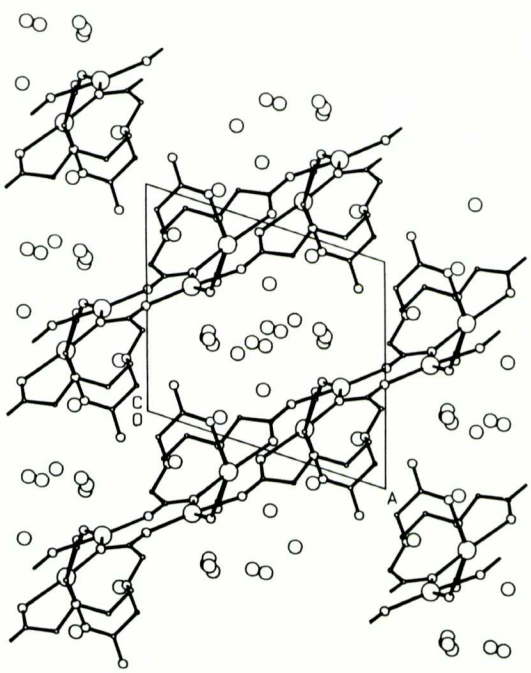

Figure 6. Projection along the b axis showing the packing scheme.

Crystal data. $C_{10}H_{14}N_2O_8Na_2(H_2O)_2$. Fw = 372, orthorhombic, **a** = 15.945(4); **b** = 9.845(3); **c** = 8.912(3). V = 1398.9(9)Å^3, Pbca, Dx = 1.77 g cm^{-3}, Z = 4, F(000) = 776, (Mo Kα) = 0.71069 Å, (Mo Kα) = 2.21 cm^{-1}. 298 K

Table 7. Positional parameters and anisotropic thermal parameters of the nonhydrogen atoms (X10000) of $(C_{10}H_{14}N_2O_8Na_2(H_2O)_2$.
The temperature factor is of the form $\exp(-2\pi\ u_{IJ}\ h_I\ h_J\ a_I^*\ a_J^*)$.
(BEQ = 8 π^2 /3 $u_{IJ}\ a_I^*\ a_J^*\ a_I.a_J$)

	X/A	Y/B	Z/C	BEQ	U11	U22	U33	U23	U13	U12
NA	11050(3)	-516(4)	5623(5)	2.00(18)	262(22)	161(23)	339(25)	-28(25)	-15(24)	29(19)
C(1)	9533(6)	-5222(11)	4930(14)	1.70(49)	97(54)	225(65)	323(66)	150(57)	-88(48)	-31(51)
N(1)	9121(5)	-4475(8)	3666(11)	1.19(34)	89(37)	83(44)	278(47)	64(53)	-47(41)	-50(39)
O(11)	9979(4)	-1063(7)	3557(9)	1.66(32)	261(36)	25(38)	343(49)	-20(37)	30(36)	-30(34)
O(12)	10323(4)	-2934(7)	2295(9)	2.29(38)	320(44)	207(45)	343(55)	-38(43)	157(35)	18(34)
C(11)	9877(6)	-2276(11)	3179(13)	1.63(51)	187(52)	167(74)	265(66)	76(59)	-52(58)	9(49)
C(12)	9116(6)	-2969(9)	3916(11)	1.53(48)	156(49)	105(62)	319(73)	-26(54)	-34(52)	-20(45)
O(21)	6986(4)	-4680(9)	2318(9)	2.60(39)	161(39)	493(55)	335(54)	41(49)	-54(38)	53(34)
O(22)	8163(4)	-4015(7)	1174(9)	1.86(33)	234(36)	161(42)	311(47)	163(40)	60(39)	-14(34)
C(21)	7765(6)	-4512(10)	2226(12)	1.47(50)	183(59)	156(60)	218(72)	-52(63)	-42(48)	15(47)
C(22)	8250(6)	-5040(11)	3590(14)	1.97(49)	155(47)	206(57)	389(81)	-11(57)	-53(59)	-63(50)
OW	11811(4)	-2177(7)	4341(9)	2.61(39)	398(49)	130(45)	462(56)	11(41)	83(43)	55(36)

Table 8. Bond distances and angles in $C_{10}H_{14}N_2O_8Na_2(H_2O)_2$

Bond distances (Å)

N(1)	---C(1)	1.497(14)	C(11)	---O(11)	1.251(12)
C(1)	---C(1)	1.557(20)	C(12)	---C(11)	1.539(14)
C(11)	---N(1)	1.499(12)	C(21)	---O(21)	1.256(12)
C(22)	---N(1)	1.498(12)	C(21)	---O(22)	1.232(12)
C(11)	---O(12)	1.243(12)	C(22)	---C(21)	1.532(14)

Bond angles (°)

C(12)	-N(1)	-C(1)	112.1(8)	C(12)	-C(11)	-O(11)	114.2(10)
C(22)	-N(1)	-C(1)	105.0(8)	C(11)	-C(12)	-N(1)	111.8(9)
C(22)	-N(1)	-C(12)	111.7(8)	O(22)	-C(21)	-O(21)	127.6(10)
C(11)	-O(11)	-NA	118.6(6)	C(22)	-C(21)	-O(21)	113.7(10)
O(11)	-C(11)	-O(12)	126.4(10)	C(22)	-C(21)	-O(22)	118.6(9)
C(12)	-C(11)	-O(12)	119.3(9)	C(21)	-C(22)	-N(1)	112.2(9)

Experimental. A prismatic crystal (0.1x0.1x02 mm) was selected and mounted on a Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 \leq \theta \leq 12$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using scan technique. 442 reflections were measured in the range $2 \leq \theta \leq 25$. 438 reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization but no absorption corrections were made.

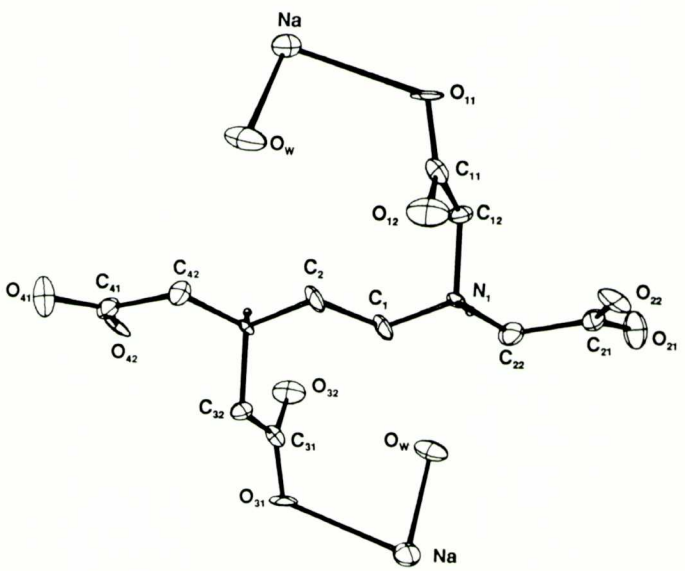

Figure 7. A stereoscopic view of the molecule $C_{10}H_{14}N_2O_8Na_2(H_2O)_2$

The structure was solved by direct methods, using SHELX76 computer program and refined by full-matrix least-squares method, with the SHELX76 computer program. The function minimized was $\Sigma\, w\, |\, |Fo| - |Fc|^2$, where $w = (\sigma^2(Fo) + 0.0048\, |\, Fo\, |^2)^{-1}$. f, f' and f'' were taken from International Tables for X-ray Crystallography. One hydrogen atom was located from a difference synthesis and the remaining hydrogen atoms were computed. All atomic coordinates were refined with an overall isotropic temperature factor, using a gliding model for computed atoms. The

final R factor was 0.049 (wR = 0.056) for all observed reflections. Number of refined parameters was 337. Max. shift/e.s.d = 0.1, Max. and min. peaks in final difference synthesis were 0.3 and -0.3 eÅ^{-3}, respectively.

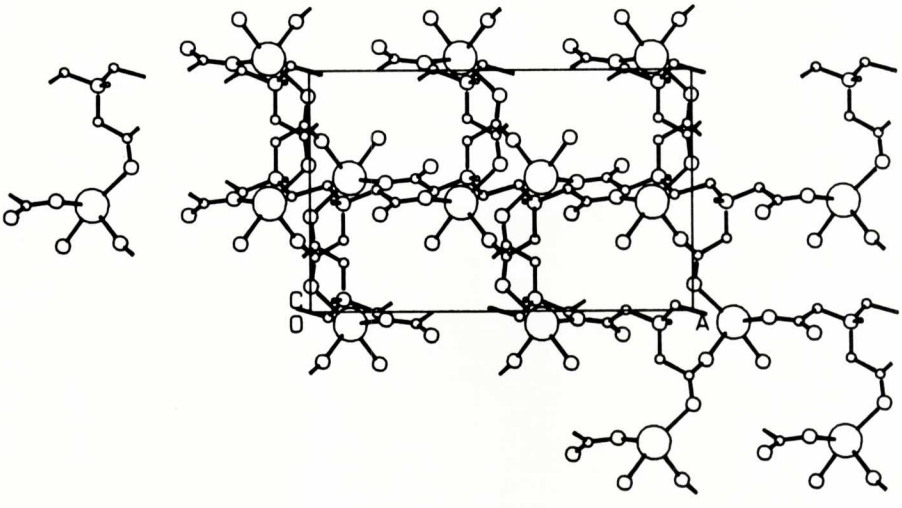

Figure 8. Projection along the b axis showing the packing scheme.

Crystal data. $[C_{10}H_{12}N_2O_8Na(Na(H_2O)_2)_2Na(H_2O)_2]2(H_2O)$. Fw = 470, triclinic, **a** = 13.326(4); **b** = 9.353(3); **c** = 8.478(3). V = 933.1(5)Å^3, P1, Dx = 1.67 g cm^{-3}, Z = 2, F(000) = 488, (Mo Kα) = 0.71069Å, (Mo Kα) = 2.41 cm^{-1}. 298 K

Experimental. A prismatic crystal (0.1x0.1x0.2 mm) was selected and mounted on a Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 \leq \theta \leq 12$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using scan technique. 2663 reflections were measured in the range $2 \leq \theta \leq 25$. 2134 reflections were assumed as observed applying the condition $I \geq 2.5\ \sigma(I)$. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization but no absorption corrections were made.

Table 9. Positional parameters and anisotropic thermal parameters of the nonhydrogen atoms (X10000) of $[(C_{10}H_{12}N_2O_8Na)(Na(H_2O))_2Na(H_2O)]2H_2O$.
The temperature factor is of the form $\exp(-2\pi\ u_{IJ}\ h_I\ h_J\ a_I^*\ a_J^*)$.
($BEQ = 8\ \pi^2\ /3\ u_{IJ}\ a_I^*\ a_J^*\ a_I.a_J$)

	X/A	Y/B	Z/C	BEQ	U11	U22	U33	U23	U13	U12
NA(1)	6029(2)	-899(2)	4233(4)	2.49(11)	105(9)	341(12)	526(22)	169(12)	134(10)	34(8)
NA(2)	8000(2)	4884(3)	9716(4)	2.88(13)	217(11)	364(13)	569(24)	190(13)	187(12)	75(9)
NA(3)	5911(2)	3154(3)	5196(4)	3.14(13)	220(11)	406(13)	644(25)	208(14)	221(12)	108(9)
NA(4)	6055(2)	3299(3)	10589(4)	3.12(13)	218(11)	462(14)	529(24)	181(14)	155(12)	75(10)
N(1)	7627(3)	-828(5)	7306(8)	2.27(24)	132(20)	245(23)	563(48)	122(26)	207(24)	55(17)
C(1)	8652(4)	-1224(6)	7178(10)	2.40(29)	147(24)	372(31)	459(55)	126(32)	175(28)	103(22)
C(2)	8800(4)	-550(6)	5748(9)	2.24(29)	104(23)	405(32)	344(54)	97(33)	95(26)	25(22)
N(2)	7846(3)	-992(5)	3996(8)	1.95(23)	153(20)	300(24)	343(43)	121(25)	140(22)	36(17)
O(11)	7064(3)	-4528(4)	6903(7)	2.72(21)	248(19)	297(21)	530(41)	182(23)	172(21)	86(16)
O(12)	5922(3)	-3224(4)	5095(7)	2.59(21)	151(18)	377(22)	444(39)	186(23)	82(19)	37(16)
C(11)	6697(4)	-3329(6)	6561(10)	2.64(31)	185(26)	302(30)	675(62)	215(34)	295(32)	45(22)
C(12)	7221(4)	-1953(6)	8024(10)	2.39(29)	249(27)	259(28)	408(56)	112(31)	137(28)	23(22)
O(21)	5841(3)	626(5)	6783(9)	5.30(29)	136(21)	510(28)	1075(62)	-95(31)	86(25)	105(19)
O(22)	6850(3)	2678(4)	8517(7)	2.99(23)	295(21)	275(22)	567(44)	87(23)	186(22)	80(16)
C(21)	6739(4)	1374(6)	7893(9)	1.91(29)	213(27)	293(31)	259(51)	142(31)	106(26)	98(22)
C(22)	7802(4)	624(6)	8339(11)	2.86(31)	178(26)	232(28)	719(64)	138(33)	220(31)	60(21)
O(31)	5844(3)	-2512(5)	1461(7)	3.45(24)	144(19)	396(24)	702(47)	26(25)	157(21)	24(16)
O(32)	6675(3)	-4257(4)	536(7)	2.92(23)	275(20)	278(22)	592(44)	72(24)	231(23)	50(16)
C(31)	6677(4)	-3143(6)	1548(10)	2.59(32)	205(27)	264(31)	570(62)	160(35)	196(30)	19(23)
C(32)	7828(4)	-2459(6)	3124(9)	2.32(29)	169(25)	291(29)	354(55)	5(31)	75(26)	44(21)
O(41)	6843(4)	1498(5)	4210(8)	3.71(28)	493(26)	400(25)	821(54)	277(29)	507(32)	199(21)
O(42)	7709(3)	2587(5)	2902(8)	3.55(24)	343(22)	402(24)	735(47)	346(27)	274(25)	56(18)
C(41)	7403(5)	1464(7)	3306(11)	2.98(33)	207(28)	361(33)	577(66)	189(37)	151(32)	64(24)
C(42)	7790(5)	28(7)	2802(11)	3.33(35)	280(29)	344(32)	840(71)	270(38)	373(37)	85(25)
OW(1)	8756(4)	4509(5)	6106(9)	4.79(29)	250(22)	568(30)	1025(59)	145(32)	311(28)	48(20)
OW(2)	9254(3)	3598(5)	11797(7)	3.54(25)	255(21)	612(29)	515(45)	234(28)	162(22)	47(19)
OW(3)	5313(3)	4262(5)	2581(7)	3.44(24)	252(20)	446(25)	734(47)	284(27)	269(24)	98(18)
OW(4)	9713(3)	6601(5)	10796(8)	3.94(26)	295(22)	548(29)6	31(49)	136(29)	180(24)	23(20)
OW(5)	5289(19)	452(24)	10178(57)	17.44(228)	977(205)	1356(257)	3315(405)	1068(305)	-185(214)	367(140)

Table 10. Bond distances and angles in $[C_{10}H_{12}N_2O_8Na(H_2O)_2)_2Na(H_2O)]2(H_2O)$

Bond distances (Å)

C(1)	---N(1)	1.472(6)	C(21)	---O(21)	1.245(7)
C(12)	---N(1)	1.491(7)	C(21)	---O(22)	1.221(7)
C(22)	---N(1)	1.436(8)	C(22)	---C(21)	1.534(6)
C(2)	---C(1)	1.536(8)	C(31)	---O(31)	1.258(6)
C(2)	---N(2)	1.457(8)	C(31)	---O(32)	1.232(8)
C(32)	---N(2)	1.439(7)	C(32)	---C(31)	1.555(8)
C(42)	---N(2)	1.485(8)	C(41)	---O(41)	1.276(8)
C(11)	---O(11)	1.270(6)	C(41)	---O(42)	1.262(7)
C(11)	---O(12)	1.253(8)	C(42)	---C(41)	1.517(8)
C(12)	---C(11)	1.526(9)			

Bond angles (º)							
C(1)	-N(1)	-NA(1)	111.4(4)	NA(4)	-O(22)	-NA(3)	122.9(2)
C(12)	-N(1)	-NA(1)	104.6(3)	C(21)	-O(22)	-NA(2)	147.8(3)
C(12)	-N(1)	-C(1)	109.4(4)	C(21)	-O(22)	-NA(3)	88.8(4)
C(22)	-N(1)	-NA(1)	107.2(3)	C(21)	-O(22)	-NA(4)	115.0(4)
C(22)	-N(1)	-C(1)	111.5(4)	O(22)	-C(21)	-O(21)	125.2(5)
C(22)	-N(1)	-C(12)	112.6(5)	C(22)	-C(21)	-O(21)	116.6(5)
C(2)	-C(1)	-N(1)	110.5(4)	C(22)	-C(21)	-O(22)	117.8(5)
N(2)	-C(2)	-C(1)	112.7(4)	C(21)	-C(22)	-N(1)	114.6(5)
C(2)	-N(2)	-NA(1)	110.9(4)	C(31)	-O(31)	-NA(1)	117.1(4)
C(32)	-N(2)	-NA(1)	106.9(3)	NA(4)	-O(32)	-NA(2)	90.6(2)
C(32)	-N(2)	-C(2)	112.7(4)	C(31)	-O(32)	-NA(2)	132.8(3)
C(42)	-N(2)	-NA(1)	104.0(3)	C(31)	-O(32)	-NA(4)	124.5(4)
C(42)	-N(2)	-C(2)	112.3(5)	O(32)	-C(31)	-O(31)	127.0(6)
C(42)	-N(2)	-C(32)	109.5(5)	C(32)	-C(31)	-O(31)	116.4(6)
N(A3)	-O(11)	-NA(1)	100.2(2)	C(32)	-C(31)	-O(32)	116.6(5)
C(11)	-O(11)	-NA(2)	127.4(5)	C(31)	-C(32)	-N(2)	114.5(4)
C(11)	-O(11)	-NA(3)	120.4(4)	NA(3)	-O(41)	-NA(1)	104.8(2)
C(11)	-O(12)	-NA(1)	115.1(3)	C(41)	-O(41)	-NA(1)	115.2(4)
O(12)	-C(11)	-O(11)	123.4(6)	C(41)	-O(41)	-NA(3)	137.0(4)
C(12)	-C(11)	-O(11)	118.1(6)	C(41)	-O(42)	-NA(4)	108.1(4)
C(12)	-C(11)	-O(12)	118.5(5)	O(42)	-C(41)	-O(41)	123.1(6)
C(11)	-C(12)	-N(1)	108.6(5)	C(42)	-C(41)	-O(41)	118.6(5)
C(21)	-O(21)	-NA(1)	112.3(4)	C(42)	-C(41)	-O(42)	118.2(6)
NA(3)	-O(22)	-NA(2)	94.5(2)	C(41)	-C(42)	-N(2)	112.5(6)
NA(4)	-O(22)	-NA(2)	89.9(2)	NA(4)	-OW(3)	-NA(3)	113.1(2)

The structure was solved by direct methods, using MULTAN80 computer program and refined by full-matrix least-squares method, with the SHELX76 computer program. The function minimized was $\Sigma\, w\, |\,|Fo| - |Fc|^2$, where $w = (\sigma^2(Fo) + 0.0048\,|\,Fo\,|^2)^{-1}$. f, f' and f'' were taken from International Tables for X-ray Crystallography. All hydrogen atoms were located from a difference synthesis. All atomic coordinates were refined with an overall isotropic temperature factor, using a gliding model for computed atoms. The final R factor was 0.063 (wR = 0.063) for all observed reflections. Number of refined parameters was 337. Max. shift/e.s.d = 0.1, Max. and min. peaks in final difference synthesis were 0.3 and -0.3 $eÅ^{-3}$, respectively.

Discussion

Metal Hydrogen Complexes:

In these structures the amino groups are protonated. The metal is

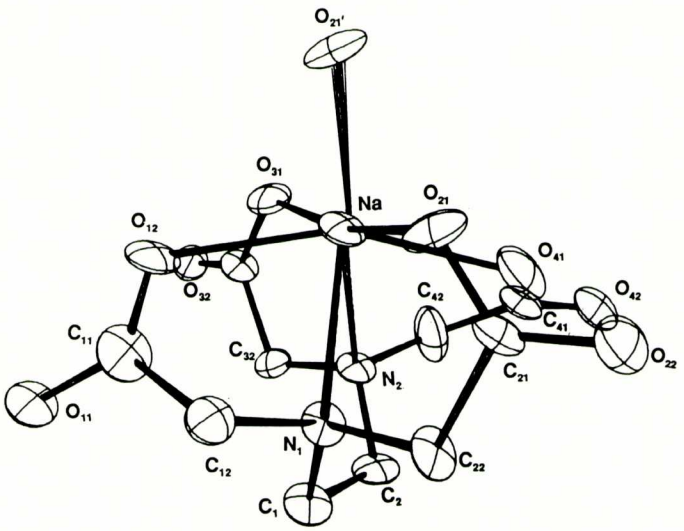

Figure 9. A stereoscopic view of the molecule $[C_{10}H_{12}N_2O_8Na(Na(H_2O)_2)_2 Na(H_2O)]2(H_2O)$

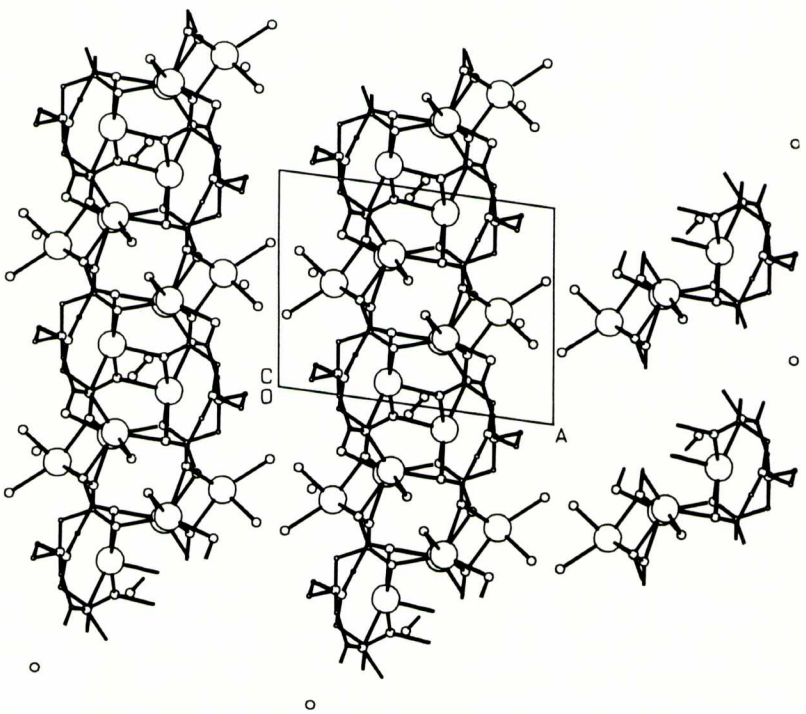

Figure 10. Projection along the b axis showing the packing scheme.

hexacoodinated and is shaped as an octahedron. The EDTA configuration is "cis".

In the first calcium structure, the metal is coordinate to four carboxylic groups from four different EDTA molecules, and two water molecules. The second one is different from the previous structure, because the metal is coordinated to five carboxylic groups of different EDTA molecules, and one water molecule.

Table 11. Bond distances and angles of coordination sphere in $[C_{10}H_{12}N_2O_8Ca(H_2O)\ Ca(H_2O)_2]2.75(H_2O)$

Bond distances (Å)			
O(21)	---CA	2.299 (7)	
OW(1)	---CA	2.376 (7)	
OW(2)	---CA	2.356 (8)	
O(11) (i)	---CA	2.297 (7)	i = 0.5-x, y-0.5, 1.5-z
O(31) (ii)	---CA	2.322 (7)	ii = x-0.5, 0.5-y, 0.5+z
O(41)(iii)	---CA	2.327 (7)	iii = 1-x, -y, 1-z

Bond angles (°)							
OW(1)	-CA	-O(21)	84.3 (3)	O(11)(i)	-CA	-OW(1)	98.6 (3)
OW(2)	-CA	-O(21)	95.5 (3)	O(31)(ii)	-CA	-OW(1)	93.9 (3)
O(11)(i)	-CA	-O(21)	175.1 (3)	O(41)(iii)	-CA	-OW(1)	88.2 (3)
O(11)(i)	-CA	-O(31)(ii)	91.4 (3)	OW(2)	-CA	-OW(1)	178.8 (3)
O(21)	-CA	-O(31)(ii)	92.3 (3)	O(11)(i)	-CA	-OW(2)	81.5 (3)
O(11)(i)	-CA	-O(41)(iii)	87.7 (3)	O(31)(ii)	-CA	-OW(2)	87.3 (3)
O(21)	-CA	-O(41)(iii)	88.5 (3)	O(41)(iii)	-CA	-OW(2)	90.5 (3)
O(31)(ii)	-CA	-O(41)(iii)	177.8 (3)				

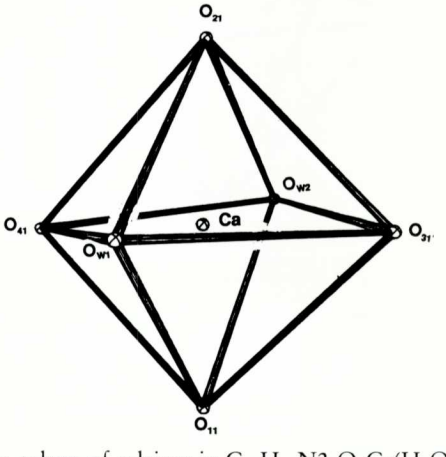

Figure 11. Coordination sphere of calcium in $C_{10}H_{14}N2_1O_8Ca(H_2O)_2$ molecule.

Table 12. Bond distances and angles of coordination sphere in $[C_{10}H_{12}N_2O_8Ca(H_2O)Ca(H_2O)_2]2.75(H_2O)$

Bond distances (Å)			
O(41)	--CA	2.398 (4)	
OW(1)	--CA	2.365 (5)	
O(11)(i)	--CA	2.256 (4)	i = 0.5+x, 0.5-y, z
O(22)(ii)	--CA	2.400 (4)	ii = 0.5-x, y-0.5, 1-z
O(21)(iii)	--CA	2.580 (4)	iii = x, y-0.5,0.5- z
O(31)(iv)	--CA	2.414 (4)	iv = 0.5-x, y, z-0.5

Bond angles (º)							
OW(1)	-CA	-O(41)	172.3(1)	O(11)(i)	-CA	-O(21)(iv)	175.1(5)
O(11)(i)	-CA	-O(41)	89.0(5)	O(22)(ii)	-CA	-O(21)(iv)	89.8(6)
O(22)(ii)	-CA	-O(41)	98.0(6)	O(41)	-CA	-O(31)(iii)	87.2(5)
O(21)(iv)	-CA	-O(41)	85.7(2)	OW(1)	-CA	-O(31)(iii)	94.1(5)
O(11)(i)	-CA	-OW(1)	98.3(5)	O(11)(i)	-CA	-O(31)(iii)	93.7(7)
O(22)(ii)	-CA	-OW(1)	80.4(6)	O(22)(ii)	-CA	-O(31)(iii)	174.6(7)
O(21)(iv)	-CA	-OW(1)	86.9(2)	O(21)(iv)	-CA	-O(31)(iii)	91.2(6)
O(22)(ii)	-CA	-O(11)(i)	82.2(7)				

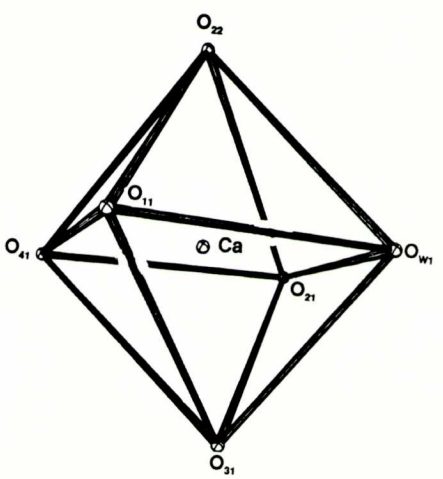

Figure 12. Coordination sphere of calcium in $C_{10}H_{14}N_2O_8Ca(H_2O)$ molecule.

The sodium protonated salt has a coordination similar to calcium protonated salts. But in this case each EDTA molecule has two sodium atoms. Also, this structure has a binary axis in the middle of the ethylenediamine group.

Table 13. Bond distances and angles of coordination sphere in $[C_{10}H_{12}N_2O_8Ca(H_2O)\ Ca(H_2O)_2]2.75(H_2O)$

Bond distances (Å)			
O(11)	--NA	2.569(8)	
OW	--NA	2.335(8)	
O(11)(i)	--NA	2.374(8)	i = x, -0.5-y, z+0.5
O(12)(ii)	--NA	2.428(8)	ii = 2-x, -y, 1-z
O(21)(iii)	--NA	2.374(8)	iii = 0.5+x, -0.5-y, 1-z
O(22)(iv)	--NA	2.515(8)	iv = 2-x, 0.5+y, 0.5-z

Bond angles (º)							
O(11)(i)	-NA	-OW	96.2(3)	O(12)(ii)	-NA	-O(21)(iii)	171.7(3)
O(11)	-NA	-O(11)(i)	89.5(3)	O(11)(i)	-NA	-O(21)(iii)	98.2(3)
OW	-NA	-O(11)	81.3(3)	O(12)(ii)	-NA	-O(22)(iv)	177.0(3)
O(11)	-NA	-O(11)(i)	83.8(3)	OW	-NA	-O(22)(iv)	80.8(3)
OW	-NA	-O(11)(i)	165.4(3)	O(11)	-NA	-O(22)(iv)	89.9(3)
O(12)(ii)	-NA	-O(11)(i)	84.2(3)	O(11)(i)	-NA	-O(22)(iv)	99.0(3)
O(11)	-NA	-O(21)(iii)	82.9(3)	O(21)(iii)	-NA	-O(22)(iv)	97.5(3)
OW	-NA	-O(21)(iii)	96.2(3)	OW	-NA	-O(12)(ii)	81.3(3)

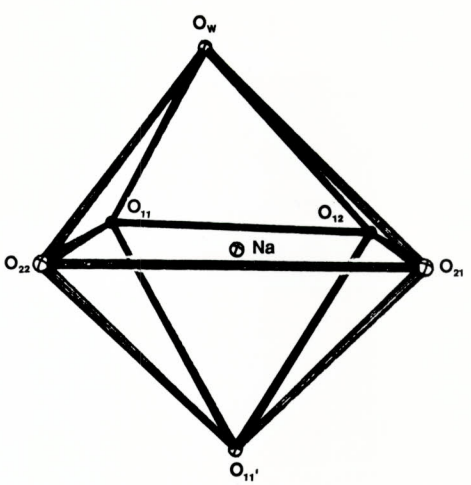

Figure 13. Coordination sphere of calcium in $C_{10}H_{14}N_2O_8Na_2(H_2O)_2$ molecule.

Metal Complexes:

These compounds are similar, but the calcium salt has two calcium atoms for one EDTA molecule and the sodium salt has four sodium atoms

for one EDTA molecule. The EDTA configuration is "cis". The structure has a polymeric configuration.

In the calcium case, the internal metal is coordianted to four carboxylic groups and two amino groups of the same EDTA molecule. Also it is coordinated with one EDTA molecule and one water molecule.

Table 14. Bond distances and angles of coordination sphere in $[C_{10}H_{12}N_2O_8Ca(H_2O)Ca(H_2O)_2]2.75(H_2O)$

Bond distances (Å)			
N(1)	--CA(1)	2.719(4)	
N(2)	--CA(1)	2.608(3)	
O(11)	--CA(1)	2.372(3)	
O(21)	--CA(1)	2.369(3)	
O(31)	--CA(1)	2.467(3)	
O(41)	--CA(1)	2.416(3)	
OW(1)	--CA(1)	2.464(4)	
O(31)(i)	--CA(1)	2.530(3)	i = 1-x, -y, 1-z
O(21)	--CA(2)	2.455(3)	
O(22)	--CA(2)	2.588(3)	
OW(2)	--CA(2)	2.254(25)	
OW(2)'	--CA(2)	2.435(24)	
OW(3)	--CA(2)	2.350(4)	
O(42)(ii)	--CA(2)	2.379(3)	ii = x, y, 1+z
O(22)(iii)	--CA(2)	2.359(3)	iii = -x, -1-y, 1-z
O(32)(i)	--CA(2)	2.322(3)	

Bond angles (º)							
N(2)	-CA(1)	-N(1)	67.0(1)	O(41)	-CA(1)	-O(31)	106.3(1)
N(2)	-CA(1)	-N(1)	67.0(1)	OW(1)	-CA(1)	-N(1)	143.9(1)
O(11)	-CA(1)	-N(1)	66.8(1)	OW(1)	-CA(1)	-N(2)	116.3(1)
O(11)	-CA(1)	-N(2)	76.1(1)	OW(1)	-CA(1)	-O(11)	148.8(1)
O(21)	-CA(1)	-N(1)	64.5(1)	OW(1)	-CA(1)	-O(21)	96.0(1)
O(21)	-CA(1)	-N(2)	129.8(1)	OW(1)	-CA(1)	-O(31)	78.4(1)
O(21)	-CA(1)	-O(11)	96.0(1)	OW(1)	-CA(1)	-O(41)	74.2(1)
O(31)	-CA(1)	-N(1)	128.5(1)	N(1)	-CA(1)	-O(31)(i)	132.2(1)
O(31)	-CA(1)	-N(2)	66.6(1)	N(2)	-CA(1)	-O(31)(i)	135.0(1)
O(31)	-CA(1)	-O(11)	81.5(1)	O(11)	-CA(1)	-O(31)(i)	78.3(1)
O(31)	-CA(1)	-O(21)	162.6(1)	O(21)	-CA(1)	-O(31)(i)	89.0(1)
O(41)	-CA(1)	-N(1)	74.8(1)	O(31)	-CA(1)	-O(31)(i)	73.6(1)
O(41)	-CA(1)	-N(2)	67.6(1)	O(31)(i)	-CA(1)	-O(41)	146.7(1)
O(41)	-CA(1)	-O(11)	134.9(1)	O(31)(i)	-CA(1)	-OW(1)	73.2(1)
O(41)	-CA(1)	-O(21)	87.7(1)				

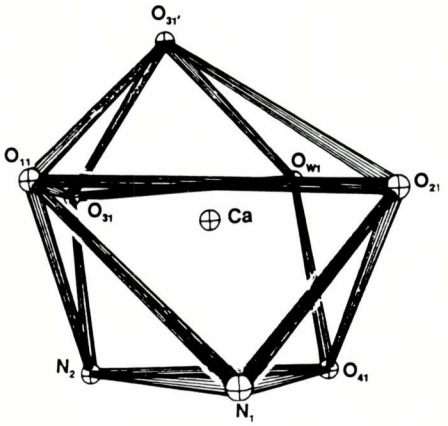

Figure 14. Coordination sphere of the inner calcium in $[C_{10}H_{12}N_2O_8Ca(H_2O)\ Ca(H_2O)_2]2.75(H_2O)$ molecule

In the sodium salt, the internal metal is also coordinated to four carboxylic groups and two amino groups of the same EDTA molecule, and with one carboxylic group from the other EDTA molecule.

Table 15. Bond distances and angles of coordination sphere in $[C_{10}H_{12}N_2O_8Ca(H_2O)\ Ca(H_2O)_2]2.75(H_2O)$

Bond distances (Å)			
N(1)	--NA(1)	2.549(6)	
N(2)	--NA(1)	2.518(4)	
O(12)	--NA(1)	2.425(4)	
O(21)	--NA(1)	2.494(7)	
O(31)	--NA(1)	2.477(6)	
O(41)	--NA(1)	2.458(4)	
O(21)(i)	--NA(1)	2.303(6)	i = 1-x, -y, 1-z
OW(2)	--NA(2)	2.387(5)	
OW(4)	--NA(2)	2.457(5)	
O(22)	--NA(2)	2.310(5)	
O(32)(iii)	--NA(2)	2.286(5)	iii = x, 1+y, 1+z
O(11)(ii)	--NA(2)	2.344(5)	ii = x, 1+y, z
O(22)	--NA(3)	2.671(6)	
O(41)	--NA(3)	2.292(5)	
OW(3)	--NA(3)	2.440(5)	
O(21)	--NA(3)	2.927	
O(12)(i)	--NA(3)	2.352(5)	i = 1-x, -y, 1-z
O(11)(ii)	--NA(3)	2.432(5)	ii = x, 1+y, z
O(22)	--NA(4)	2.419(5)	
OW(5)	--NA(4)	2.722(5)	
O(31)(i)	--NA(4)	2.368(5)	i = 1-x, -y, 1-z
O(32)(iii)	--NA(4)	2.414(4)	iii = x, 1+y, 1+z
O(42)(iv)	--NA(4)	2.449(5)	iv = x, y, 1+z
OW(3)(iv)	--NA(4)	2.374(6)	

Bond angles (º)							
N(1)	-NA(1)	-N(2)	70.4	NA(1)	-N(1)	-O(12)	52.8
N(1)	-NA(1)	-O(12)	70.3	N(2)	-N(1)	-O(12)	80.8
N(2)	-NA(1)	-O(12)	98.7	NA(1)	-N(1)	-O(21)	56.7
N(1)	-NA(1)	-O(21)	64.6	N(2)	-N(1)	-O(21)	103.7
N(2)	-NA(1)	-O(21)	123.8	O(12)	-N(1)	-O(21)	82.4
O(12)	-NA(1)	-O(21)	96.4	NA(1)	-N(2)	-N(1)	55.3
N(1)	-NA(1)	-O(21)(i)	134.0	NA(1)	-N(2)	-O(31)	56.0
N(2)	-NA(1)	-O(21)(i)	154.7	N(1)	-N(2)	-O(31)	103.0
O(12)	-NA(1)	-O(21)(i)	96.9	NA(1)	-N(2)	-O(41)	55.4
O(21)	-NA(1)	-O(21)(i)	73.7	NA(1)	-N(2)	-O(41)	76.9
N(1)	-NA(1)	-O(31)	123.7	O(31)	-N(2)	-O(41)	90.7
N(2)	-NA(1)	-O(31)	66.5	NA(1)	-O(12)	-N(1)	56.9
O(12)	-NA(1)	-O(31)	82.1	NA(1)	-O(21)	-N(1)	58.7
O(21)	-NA(1)	-O(31)	169.7	NA(1)	-O(21)	-O(21)(i)	50.1
O(21)(i)	-NA(1)	-O(31)	96.3	N(1)	-O(21)	-O(21)(i)	106.3
N(1)	-NA(1)	-O(41)	89.7	NA(1)	-O(21)	-O(41)	49.3
N(2)	-NA(1)	-O(41)	67.1	N(1)	-O(21)	-O(41)	73.1
O(12)	-NA(1)	-O(41)	158.8	O(21)(i)		-O(21)	-O(41) 74.9
O(21)	-NA(1)	-O(41)	80.4	NA(1)	-O(31)	-N(2)	57.5
O(21)(i)	-NA(1)	-O(41)	102.2	NA(1)	-O(41)	-N(2)	57.5
O(31)	-NA(1)	-O(41)	104.6	NA(1)	-O(41)	-O(21)	50.3

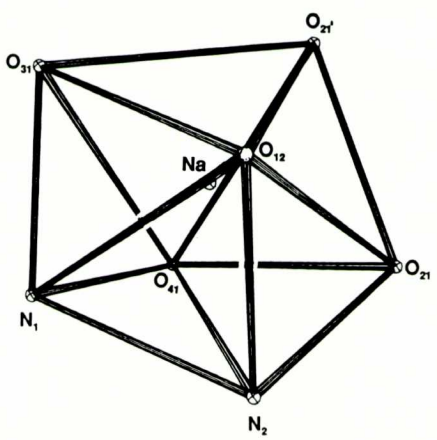

Figure 15. Coordination sphere of the inner sodium in $[C_{10}H_{12}N_2O_8Na(Na(H_2O)_2)_2Na(H_2O)]2(H_2O)$ molecule.

An important feature of these structures is the protonation groups, since, all the structures with protonated EDTA are coordinated with the metal to the nitrogen atoms, and the metal is located in the internal position. But in our structures the amino groups are protonated and the metal is coordinated with the carboxylic group. Metal position is surrounded by oxygens atoms belonging to four EDTA molecules.

The nonprotonated structures are the same in all the cases. One metal has an internal position and the others are located outside the EDTA molecule.

Abstract

The structural characteristics of calcium and sodium salts of the ethylenediaminetetraacetic acid (EDTA) have been studied by single crystal X-ray diffraction. We have studied all the calcium and sodium salts of ethylenediaminotetraacetate which are obtained at different pH. In our laboratory three different crystals of the calcium salts were obtained: two of them had one calcium atom for an EDTA molecule, they are protonated; and the third one had two calcium atoms for one EDTA molecule. There were two different crystals of sodium salts: one was a protonated salt and one was a non protonated sodium salt.

REFERENCES

1. Main, P., Fiske, S.J.; Hull, S.E., Lessinger, L., Germain, G., Declerq, and J.P., Woolfon, M.M., MULTAN 80. A system of computer programs for crystal structure determination from X-ray diffraction data. York University, England and Louvain University, Belgium (1980).
2. Shelxdrick, G.M., A program for crystal structure determination. Cambridge University, England (1976).
3. Johnson, C.K., ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessy (1965).
4. Motherwells, S., and Clegg, B., Program for plotting molecular and crystal structures (1978).