Acta Cryst. (1972). B28, 1914

The Crystal Structure of Calcium Nitrilotriacetate Dihydrate

BY SIMON H. WHITLOW

Inland Waters Branch, Department of the Environment, Ottawa, Canada

(*Received* 25 *October* 1971)

Calcium nitrilotriacetate dihydrate, $Ca.HN^+(CH_2COO^-)_3.2H_2O$, is monoclinic with $a=11{\cdot}374$ (1), $b=9{\cdot}730$ (1), $c=10{\cdot}107$ (1) Å, $\beta=115{\cdot}34$ (2)°, space group $P2_1/c$ with four formula units in the unit cell. The positional and anisotropic thermal parameters have been refined from diffractometer data to an R value of 0·037 for 2680 reflexions. Each nitrilotriacetate (NTA) group is protonated at the nitrogen atom and is bonded to neighbouring calcium atoms through five of the six carboxylic oxygen atoms, with Ca–O distances of 2·316 to 2·560 (5) Å. The sixth oxygen atom forms a hydrogen bond of 2·767 Å with one of the two water molecules coordinated to each calcium ion. At every calcium there is a seven-fold coordination of oxygen atoms in a pentagonal bipyramidal configuration but in no case are there multidentate interactions between an NTA group and a particular calcium atom.

Introduction

To decrease the rate of eutrophication in the Great Lakes, recent emphasis has been placed on the removal of phosphates from sewage discharge. The Canadian Government under the Canada Water Act has implemented a partial ban on the phosphate content of detergents since it is estimated (*International Joint Commission Report*, 1969) that more than half of the phosphates in domestic sewage come from washing products. The regulations in Canada, which at present limit the phosphate content to 20%, are designed as an interim measure while suitable waste treatment plants for more complete nutrient removal can be constructed. A possible replacement for phosphates as a sequestering agent is nitrilotriacetic acid (NTA). With three carboxylate groups and a nitrogen atom as potential nucleophilic sites, NTA is recognized as a strong chelating agent.

The purpose of this structure analysis was to investigate the interactions between NTA and a divalent metal atom. The calcium salt was selected because the Ca^{2+} ion is the principal ion which must be sequestered for effective washing. Since NTA can theoretically behave as a tri- or tetradentate ligand, the nature of the metal–chelate interactions including the possibility of a metal–nitrogen bond are of considerable interest.

Experimental

Calcium nitrilotriacetate dihydrate, $Ca.HN^+(CH_2COO^-)_3.2H_2O$, was prepared by combining NTA and $CaCO_3$ in aqueous solution. While detergent washing is generally done in an alkaline solution, in these conditions there is considerable hydrolysis of the NTA ion. The one-metal to one-NTA complex, which is stable to about a pH of 9, becomes the principal species in acid solution (Ramamoorthy, Guarnaschelli & Fecchio, 1971), and formation of this predominant unhydrolysed complex was promoted by maintaining the pH at about 6 during the preparation. Colourless prisms were crystallized from water. One of these crystals ground to a sphere of 0·30 mm diameter was used for the intensity measurements. The sphere was mounted in a random orientation on a four-circle computer-controlled diffractometer (Gabe, Alexander & Goodman, 1970). The orientation matrix and lattice parameters were refined by least squares from the optimum angular settings of 20 reflexions aligned by computer control. For these measurements a small counting aperture was used with a take-off angle of 1° and a graphite monochromator (Mo $K\alpha_1=0{\cdot}70926$ Å).

The unit-cell constants were determined as:

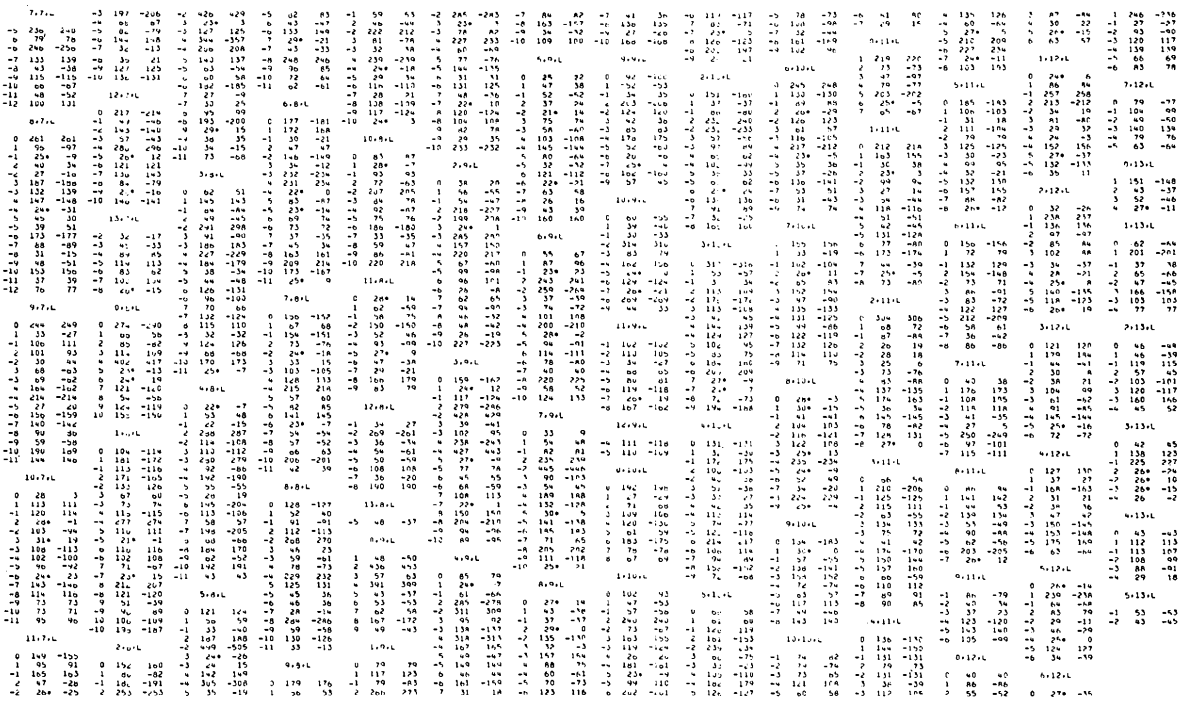
$a=11{\cdot}374(1)$, $b=9{\cdot}730(1)$, $c=10{\cdot}107(1)$ Å, $\beta=115{\cdot}34(2)°$ $V=1010{\cdot}91$ Å^3, $M=265{\cdot}24$, $F(000)=552$, $Z=4$, $D_m=1{\cdot}742$ (flotation), $D_c=1{\cdot}738$ g.cm^{-3}.

The systematic absences $l=2n+1$ for $h0l$ and $k=2n+1$ for the $0k0$ reflexions uniquely specify the space group $P2_1/c$. Intensity data for 2960 independent reflexions were collected using the θ–2θ scan technique (to a limit of $\sin\theta=0{\cdot}5$) with background readings taken before and after each integrated count and standard reflexions recorded for scaling purposes every 25 measurements. During the data collection the crystal remained stable and the standard reflexions, which fluctuated less than 5%, showed no variation with time. Lorentz and polarization factors were applied but absorption effects were negligible. With Mo $K\alpha$ radiation the linear absorption coefficient is 6·34 cm^{-1}, and for a sphere of 0·3 mm the μR value is only 0·1. Least-squares weights based on counting statistics and instrument stability were assigned to the reflexions and, where the net count was less than the 10% significance level, the reflexions were classified as unobserved and were assigned intensities equal to the threshold value. 2680

Table 1. *Observed and calculated structure factors* (× 10)

Asterisks indicate unobserved reflexions, *E*'s denote extinction.

Table 1 (*cont.*)



reflexions (95% of those measured) were considered to be observed at this significance level.

Most of the computations required in the analysis were done using the X-RAY 70 system of crystallographic programs (Stewart, Kundell & Baldwin, 1970). The structure was solved from the Patterson function, and then Fourier and difference Fourier summations together with full-matrix least-squares refinement led to the positioning of all the atoms. The form factors used were those for neutral atoms (Doyle & Turner, 1968).

The progress of the refinement is indicated by the agreement factor $(\sum||F_o|-|F_c||/\sum|F_o|)$ at various stages: after isotropic refinement of all non-hydrogen atoms, $R=0{\cdot}092$, anisotropic refinement of these atoms, $R=0{\cdot}061$, inclusion of the hydrogen atoms, $R=0{\cdot}041$, and refinement of the hydrogen atoms, $R=0{\cdot}039$. At this stage it became apparent that a number of reflexions with high $|F_o|$ values had been underestimated because of secondary extinction. One measurement (5,3,−4), judged to be in error, was removed and ten strong reflexions with $|F_o-|F_c||/F_o>0{\cdot}045$ were excluded

Table 2. *Final positional coordinates* ($\times 10^5$) *and anistropic thermal parameters* ($\times 10^4$) *for the non-hydrogen atoms*

The temperature expression is of the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+\ \ldots\ +2U_{23}klb^*c^*\cos\alpha^*)]$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	14943 (3)	−19392 (3)	90425 (3)	169 (1)	122 (1)	151 (1)	0 (1)	75 (1)	−3 (1)
N	28383 (11)	18360 (13)	65975 (13)	139 (6)	166 (6)	169 (6)	−1 (5)	70 (5)	9 (5)
C(1)	18832 (14)	8918 (15)	54941 (16)	165 (7)	197 (7)	149 (7)	−28 (6)	52 (6)	−16 (6)
C(2)	16244 (14)	−3285 (15)	62756 (17)	141 (7)	169 (7)	218 (7)	4 (6)	93 (6)	−3 (6)
C(3)	27335 (15)	32861 (15)	60589 (18)	196 (8)	155 (7)	299 (9)	−2 (6)	138 (7)	45 (6)
C(4)	15804 (14)	40206 (15)	61252 (16)	155 (7)	159 (7)	146 (7)	−15 (6)	47 (6)	−13 (6)
C(5)	41841 (15)	12673 (17)	71317 (18)	141 (7)	238 (8)	252 (8)	36 (6)	64 (6)	−16 (7)
C(6)	51164 (15)	18895 (19)	85856 (18)	187 (8)	309 (9)	233 (8)	3 (7)	68 (6)	−17 (7)
O(1)	12836 (12)	−14154 (12)	55834 (13)	371 (7)	200 (6)	364 (7)	−75 (5)	208 (6)	−98 (5)
O(2)	17406 (11)	−1222 (11)	75612 (12)	330 (7)	200 (6)	226 (6)	−13 (5)	172 (5)	11 (5)
O(3)	9331 (11)	33964 (11)	66626 (13)	235 (6)	216 (6)	302 (6)	12 (5)	169 (5)	63 (5)
O(4)	14097 (10)	52301 (11)	56515 (12)	212 (6)	148 (5)	247 (6)	−2 (4)	109 (5)	21 (4)
O(5)	46392 (12)	25445 (17)	92890 (14)	219 (7)	794 (11)	334 (7)	51 (7)	80 (6)	−251 (8)
O(6)	62912 (11)	16517 (15)	89341 (13)	156 (6)	547 (9)	309 (7)	52 (6)	36 (5)	−106 (6)
O(W1)	29941 (11)	−33891 (15)	85516 (13)	228 (6)	594 (9)	276 (7)	30 (6)	87 (5)	−151 (6)
O(W2)	1496 (11)	−33659 (12)	70713 (13)	261 (6)	302 (7)	316 (7)	−85 (5)	184 (5)	−137 (5)

from the refinement. The final R value is 0·037 with a weighted residual R_w, of 0·031 for 2680 observed reflexions. At the conclusion of refinement the calculated shifts were all comparable to or less than the estimated error. A final list of structure factors is given in Table 1, and the refined positional and thermal parameters are tabulated in Tables 2 and 3.

Table 3. *Final fractional coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2) *for the hydrogen atoms*

	x	y	z	B
H(N)	2644 (20)	1896 (21)	7376 (23)	2·6 (5)
H(Cl)	1088 (19)	1361 (20)	4955 (20)	1·8 (4)
H(C2)	2208 (17)	609 (19)	4864 (19)	2·3 (4)
H(C3)	2684 (18)	3242 (20)	5093 (20)	2·2 (4)
H(C4)	3518 (19)	3712 (21)	6666 (22)	2·8 (5)
H(C5)	4467 (18)	1389 (20)	6376 (20)	2·5 (4)
H(C6)	4121 (19)	255 (21)	7334 (21)	3·0 (5)
H(*W*1)	3808 (25)	−3173 (27)	9174 (29)	6·3 (7)
H(*W*2)	3059 (26)	−3466 (27)	7777 (30)	6·5 (7)
H(*W*3)	−351 (22)	−3814 (25)	7279 (25)	4·9 (6)
H(*W*4)	434 (26)	−3905 (28)	6611 (28)	6·2 (7)

Discussion

The principal features of the Ca–NTA interactions are the lack of a Ca–N bond (no Ca–N approach less than 3·5 Å), and the disposition of the Ca–O bonds, (Fig. 1). Although 5 of the 6 NTA oxygen atoms are bound to calcium atoms, each one is joined to a different calcium. In this compound, therefore, there is no real chelation effect where a metal atom is held by bonds to several atoms of a polydentate complexing agent. The situation here can be contrasted with the case of $Na_3NTA.3H_2O$ (Daly, 1967) in which there is a metal–nitrogen bond in addition to several metal–oxygen bonds between NTA and each Na^+ ion. It is very different also from the only other NTA–metal complex for which a structure analysis has been reported: the bisnitrilotriacetatozirconate(IV) ion (Hoard, Willstadter & Silverton, 1965). In this there are two NTA anions about the zirconium ion in a dodecahedral coordination with pairs of Zr–O bonds and weaker Zr–NH contacts.

The 11 hydrogen atoms were readily located from a final difference Fourier synthesis. Sections of the $\Delta\varrho$ map omitting the hydrogen contributions are shown in Fig. 1. Apart from these hydrogen positions there were no other fluctuations greater than $\pm 0{\cdot}3$ e.Å^{-3}. The identification of NH^+ provides evidence for the zwitterion structure assigned by Stanford (1967) to crystalline H_3NTA and suggested earlier by Chapman, Lloyd & Prince (1963) for NTA in solution. Bond

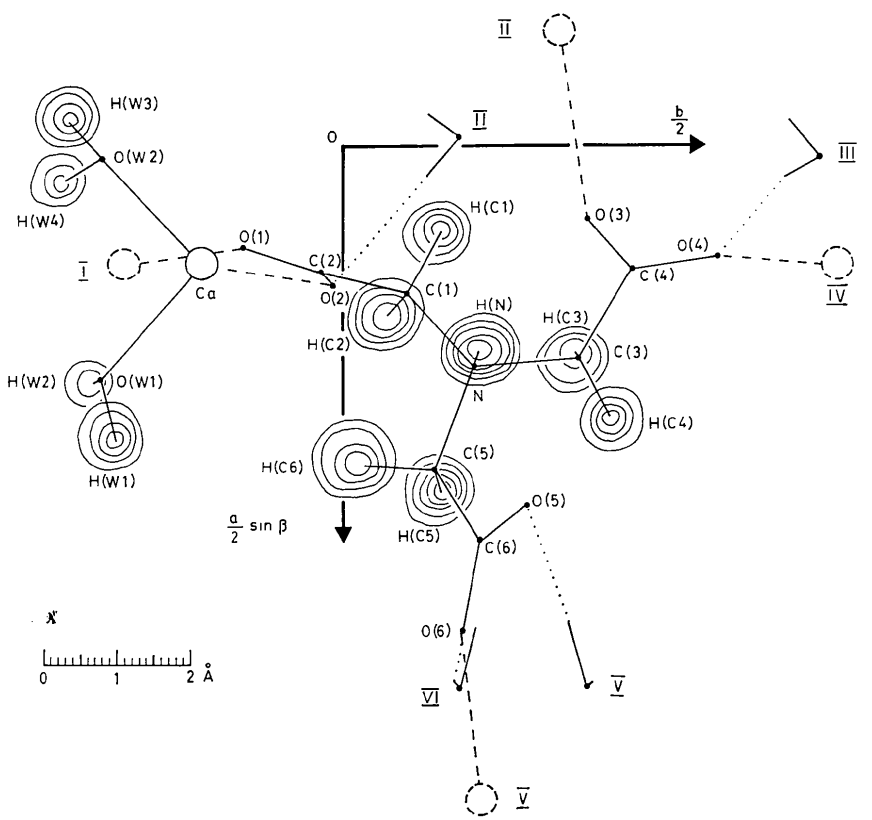


Fig. 1. A view of the structure showing hydrogen atoms (0·1 e.Å^{-3} contours from 0·4 e.Å^{-3}), hydrogen bonding (dotted lines), and Ca–O contacts (broken lines). The positions related by symmetry and unit-cell translations are: I, x, $-y-\frac{1}{2}$, $z-\frac{1}{2}$; II, $-x$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$; III, x, $y+1$, z; IV, x, $-y+\frac{1}{2}$, $z-\frac{1}{2}$; V, $-x+1$, $-y$, $-z+2$; and VI, $-x+1$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$.

lengths involving hydrogen are supplied in Table 4. The average C–H and O–H distances are 0·95 (2) and 0·84 (3) Å respectively. Hydrogen atoms bonded to different atom types show varying thermal parameters (Table 3) and angles at carbon, oxygen and nitrogen involving hydrogen approximate the expected values. The shortest hydrogen bond formed (O···O distance = 2·767 Å, O–H···O angle = 168·2°) is between O(5) of the NTA anion (the only oxygen atom not bonded to calcium), and a neighbouring water molecule. Other hydrogen bonds join three more of the NTA oxygen atoms to the water molecules through the three remaining hydrogen atoms (Fig. 1 and Table 4). The O–H···O angles range from 164·3 to 169·6° in these contacts. The remainder of the O···O contacts less than 3·0 Å [O($W2$)···O(3) at $-x$, $y-\frac{1}{2}$, $-z+\frac{3}{2}$, O($W1$)···O(6) at $-x+1$, $-y$, $-z+2$, and O($W1$)···O($W2$) of 2·728, 2·865, and 2·926 Å respectively] are unlikely to be hydrogen bonded because of the small O–H···O angles (90, 108, and 92°) which would be required if the hydrogen atoms were shared.

Table 4. *Bond lengths and distances involving hydrogen atoms*

Bond lengths (σ=0.03)		Hydrogen bond distances	
H(N)—N	0·91 Å	O(2)···H($W3^{i}$)	2·09 Å
H(C1)—C(1)	0·95	O(2)···O($W2^{i}$)	2·892
H(C2)—C(1)	0·91	O(4)···H($W4^{ii}$)	1·95
H(C3)—C(3)	0·95	O(4)···O($W2^{ii}$)	2·782
H(C4)—C(3)	0·94	O(5)···H($W1^{iii}$)	1·89
H(C5)—C(5)	0·96	O(5)···O($W1^{iii}$)	2·767
H(C6)—C(5)	1·02	O(6)···H($W2^{iv}$)	2·16
H($W1$)–O($W1$)	0·89	O(6)···O($W1^{iv}$)	2·953
H($W2$)–O($W1$)	0·82	i $-x$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$	
H($W3$)–O($W2$)	0·81	ii x, $y+1$, z	
H($W4$)–O($W2$)	0·85	iii $-x+1$, $-y$, $-z+2$	
		iv $-x+1$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$	

Short intramolecular contacts	
N···O(2)	2·769 Å
H(N)···O(2)	2·26
N···O(3)	2·670
H(N)···O(3)	2·29
N···O(5)	2·702
H(N)···O(5)	2·35

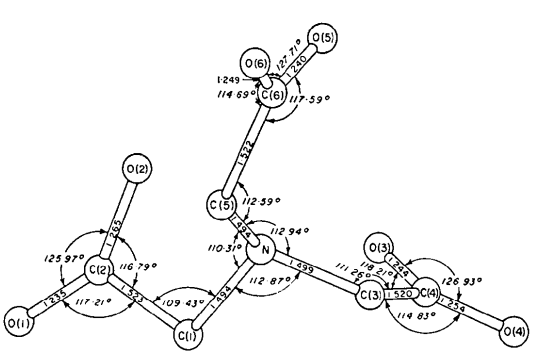


Fig. 2. The nitrilotriacetate anion (omitting hydrogen atoms) showing bond lengths (Å) and valency angles.

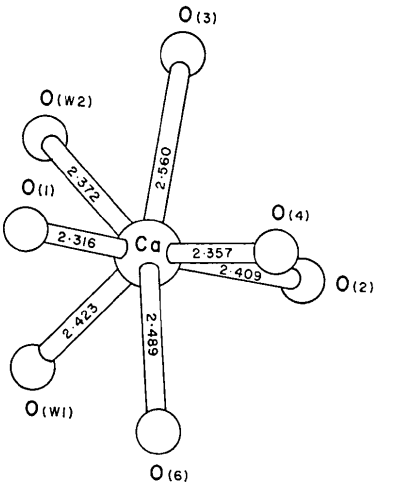


Fig. 3. The pentagonal bipyramidal calcium coordination [O(1) and O(2), apices] showing Ca–O bond lengths (Å).

The NTA anion is depicted in Fig. 2 with the calculated interatomic bond lengths and angles. The bond lengths (uncorrected for thermal vibration) and valency angles have standard deviations estimated from the least-squares matrix of about 0·005 Å and 0·20°. The structure of the anion is very similar to the descriptions given for H_3NTA (Stanford, 1967) and $Na_3NTA.3H_2O$ (Daly, 1967). In each case the $-CCO_2$ groups are planar although in $CaNTA.2H_2O$ these are more twisted with respect to each other (average angle 76·52°) than in H_3NTA (66·39°) or $Na_3NTA.3H_2O$ (60·74°). Equivalent C–N and C–C bond lengths in the anion are very consistent, the averages being 1·496 (3) and 1·522 (2) Å respectively. The C–O bond lengths, however, vary more about the average of 1·248 (11) Å, especially those at C(2). This can probably be attributed to the unique positions of O(1) and O(2) at the apices of the pentagonal bipyramid about calcium.

The calcium coordination showing the arrangement of the surrounding oxygen atoms and the Ca–O bond lengths (σ = 0·005 Å) is given in Fig. 3, the appropriate angles and the designation of the oxygen equivalent positions are supplied in Table 5. This arrangement about a seven-coordinate calcium ion is not unusual; for example similar configurations occur in calcium 1-naphthyl phosphate trihydrate (Li & Caughlan, 1965) and calcium 1,3-diphosphorylimidazole (Beard & Lenhert, 1968). One indication of the regularity of the pentagonal bipyramid is the average angle between the axial bonds and the other five atoms. In $CaNTA.2H_2O$ the average is 90·0°. There is no differentiation at calcium between the water oxygens and oxygen atoms of the NTA anion; the distances between the water molecules and calcium lie close to an average value of 2·418 (83) Å. The large standard deviation of this average indicates that the Ca–O bond is somewhat variable and is not constrained to a fixed length. In $Ca(C_{10}H_7HPO_4)_2.3H_2O$ (Li & Caughlan,

Table 5. *Bond angles* (°) *about calcium*

	O(1^{i})	O(2)	O(3^{ii})	O(4^{iii})	O(6^{iv})	O(*W*1)	O(*W*2)
O(1^{i})	–	176·37	82·28	88·70	83·39	91·13	86·88
O(2)	–	–	97·57	87·76	94·71	91·18	96·44
O(3^{ii})	–	–	–	75·19	143·70	141·93	67·05
O(4^{iii})	–	–	–	–	71·31	142·41	142·23
O(6^{iv})	–	–	–	–	–	71·35	144·86
O(*W*1)	–	–	–	–	–	–	75·20

Symmetry operations

i $x, -y-\frac{1}{2}, z+\frac{1}{2}$ ii $-x, y-\frac{1}{2}, -z+\frac{3}{2}$
iii $x, -y+\frac{1}{2}, z+\frac{1}{2}$ iv $-x+1, -y, -z+2$

1965) the two shortest Ca–O distances are to axial oxygen atoms. In the present structure the shortest contact is to the apical O(1) but the other unique oxygen O(2) has a more average value. The range of Ca–O contacts (2·316–2·560 Å) is considerably larger than in $Ca(C_{10}H_7HPO_4)_2.3H_2O$ (2·35–2·45 Å) but smaller than in $Ca_{1.5}C_3H_3N_2(PO_3)_2.6H_2O$ (Beard & Lenhert, 1968; 2·27–2·64 Å) and other compounds where there are bidentate oxygen atoms. Within the confines of an approximate pentagonal bipyramid the Ca–O contacts are apparently flexible and primarily determined by close packing considerations and possible hydrogen-bonding interactions.

The possibility of a furcated hydrogen bond in this structure requires consideration. Chapman, Lloyd & Prince (1963) report that the infrared spectrum of NTA in aqueous solution shows that all the three CO_2^- groups are equally bonded to NH^+ and suggest that this is equivalent to a trifurcated hydrogen bond. An intramolecular bifurcated bond has also been suggested by Stanford (1967) from N–O contact distances and a surmised hydrogen position in the structure analysis of H_3NTA. In $K.EDTA.4H_2O$ also, there are similarly three close intramolecular approaches of oxygen to NH^+ (Cotrait, 1969, average distance = 2·70 Å). As shown in Table 4 the proton on the nitrogen atom in $CaNTA.2H_2O$ is symmetrically placed between the three potential acceptors, O(2), O(3) and O(5). The observed N–O distances are all 0·2 Å less than the van der Waals sum (2·9 Å) and the H···O distances are about 0·3 Å less than the sum of the ionic radii (2·6 Å) so that the assignment of a trifurcated hydrogen bond is tempting. However, the average N–H···O angle is only 105° and it is probably more realistic to consider the close approaches to be due to steric or electrostatic factors with the hydrogen atom located at a minimum energy position.

The author is grateful to Drs E. J. Gabe and S. R. Hall of the Mines Branch, Department of Energy, Mines and Resources for assistance with the data collection and in the operation of the X-RAY 70 system of computing programs.

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