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# Structures of Sodium Zinc Nitrilotriacetate Monohydrate (173 K) and Disodium Hydrogen Nitrilotriacetate (293 K)

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## Abstract

$NaZn(C_6H_6NO_6).H_2O$: $M_r = 295{\cdot}44$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}869\,(4)$, $b = 9{\cdot}783\,(6)$, $c = 12{\cdot}292\,(6)$ Å, $V = 946{\cdot}3$ Å$^3$, $Z = 4$, $D_x = 2{\cdot}07$ g cm$^{-3}$, $\lambda$ (Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 27{\cdot}4$ cm$^{-1}$. Final $R = 0{\cdot}052$ for 859 unique reflections. The nitrilotriacetate ion is coordinated to the $Zn^{2+}$ ion in a tetradentate fashion. The remaining two octahedral sites about the $Zn^{2+}$ ion are occupied by O atoms of different nitrilotriacetate ions. A comparison of the structure with other published structures identifies a common geometry, termed the 'butterfly' geometry, for transition-metal complexes with nitrilotriacetate ligands. The $Na^+$ ions bridge the nitrilotriacetatozinc ions thereby holding the structure intact. The water molecule is coordinated to the five-coordinate $Na^+$ ion. $Na_2(C_6H_7NO_6)$: $M_r = 235{\cdot}10$, cubic, $P2_13$, $a = 9{\cdot}417\,(2)$ Å, $V = 835{\cdot}1$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}87$ g cm$^{-3}$, $\lambda$(Cu $K\bar{\alpha}$) = 1·54178 Å, $\mu = 23{\cdot}3$ cm$^{-1}$. Final $R = 0{\cdot}034$ for 208 unique reflections. The structure is the first observation of the zwitterionic form of the nitrilotriacetate ion as a tridentate chelating ion. The $[C_6H_7NO_6Na]^-$ ions are linked together by a complex network of bridging $Na^+$ ions. The differences in the coordination of the nitrilotriacetate ligand to the metal ions in these structures illustrate the versatile, multidentate chelating capabilities of the ligand.

## Introduction

The nitrilotriacetate ion, hereinafter referred to as NTA, is a versatile chelating ion and finds use as a complexing agent in industrial (Rompp, 1958) and laboratory (Schwarzenbach, Kampitsch & Steiner, 1945; Schwarzenbach, Ackermann & Ruckstuhl, 1949; Schwarzenbach & Freitag, 1951) processes. The stability constants of many NTA complexes have been determined and tabulated (Sillen & Martell, 1964). The crystal structures of the triprotic acid (Stanford, 1967), the monohydrated trisodium salt (Daly, 1967) and a variety of metal–NTA complexes (Barnett & Uchtman, 1979; Battaglia, Corradi & Tani, 1975; Butcher & Penfold, 1976; Fomenko, Kopaneva, Porai-Koshits & Polynova, 1974; Fomenko, Polynova & Porai-Koshits, 1975*a*, *b*; Hoard, Silverton & Silverton, 1968; Martin & Jacobsen, 1972; Whitlow, 1972, 1973; Wieghardt, Quiltzsch, Weiss & Nuber, 1980) have been reported. The versatility of the NTA ion as a sequestering agent prompted our investigation of the title compounds. The structures further illustrate the diversity of coordination complexes that the NTA ligand can form.

An additional purpose for the structural study of the $NaZnNTA.H_2O$ complex concerned the coordination geometry about the $Zn^{2+}$ ion. In complexes with aminocarboxylate ligands the $Zn^{2+}$ ion can assume a broad range of coordination environments – square pyramidal in the glutamatozinc(II) dihydrate structure (Gramaccioli, 1966), trigonal bipyramidal in the bis(*S*-methyl-L-cysteinato)zinc(II) structure (de Meester & Hodgson, 1977), intermediate between square pyramidal and trigonal bipyramidal in the bis(L-serinato)zinc(II) structure (van der Helm, Nicholas & Fisher, 1970), octahedral in the bis(L-methionato)zinc(II) structure (Wilson, de Meester & Hodgson, 1977) and tetrahedral in the bis(L-histidinato)zinc(II) dihydrate structure (Kistenmacher, 1972). The crystal structure analysis of $NaZnNTA.H_2O$ defines the coordination geometry about the $Zn^{2+}$ ion in the complex.

## Experimental

General experimental details are given in Table 1. All X-ray measurements were made on a Syntex $P2_1$ diffractometer equipped with an incident-beam graphite monochromator and an LT-1 low-temperature device. Lattice parameters were obtained by a least-squares analysis of 15 general reflections for each compound. The atomic scattering factors (including $f'$ and $f''$ corrections for Na and Zn) were taken from Ibers & Hamilton (1974). To determine the proper choice of enantiomer for $NaZnNTA.H_2O$, the coordinates were inverted and the refinement was repeated yielding $R = 0{\cdot}062$ ($wR = 0{\cdot}045$). Based on the *R*-factor-ratio method (Hamilton, 1964), the possibility that the second enantiomer is correct can be rejected at the 0·5% probability level; thus the parameters listed in Table 2 are the final values from the first refinement.

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Table 1. *Additional crystal data and refinement results*

| | $NaZnNTA.H_2O$ | $Na_2HNTA$ |
|---|---|---|
| Crystal dimensions (mm) | $0·03 \times 0·05 \times 0·15$ | $0·27 \times 0·25$* |
| Crystal color | Colorless | Colorless |
| Temperature (K) | 173 | 293 |
| Data-collection range | $2·0° \le 2\theta \le 53·0°$ | $8·0° \le 2\theta \le 110·0°$ |
| Scan mode | $\theta$–$2\theta$ | $\theta$–$2\theta$ |
| Scan speed | Variable, 4·0 to 29·3° $min^{-1}$ | Variable, 4·0 to 29·3° $min^{-1}$ |
| Range of $h$; $k$; $l$ | 0–10; 0–12; 0–15 | 0–10; 0–10; 0–10 ($h < k$) |
| Standard reflections measured | 002, 020, 600 | 004, 040, 400 |
| Intensity variation | Random, ≤5% relative | Random, ≤2% relative |
| Unique reflections measured | 1160 | 346 |
| Unique reflections used | 859 | 208 |
| Significance criterion | $I > 1·96\sigma(I)$ | $I > 1·96\sigma(I)$ |
| Absorption correction | None | Empirical from $\psi$ scans |
| Min., max. transmission factors | | 0·71, 1·00 |
| Structure solution | Heavy-atom method | Direct methods |
| Least-squares-refinement (on $F$) results | $R = 0·052$<br>$R_w = 0·054$<br>$S = 1·00$<br>$F(000) = 592$ | $R = 0·034$<br>$R_w = 0·038$<br>$S = 0·92$<br>$F(000) = 480$ |
| Weighting function | $[\sigma^2(\lvert F_0\rvert) + 0·001\lvert F_0\rvert^2]^{-1}$ | $\sigma^{-2}(\lvert F_0\rvert)$ |
| H-atom treatment | Fixed at idealized locations | Fixed at $\Delta\rho$ locations |
| Max. $\Delta/\sigma$ in final refinement cycle | 0·2 | 0·01 |
| Final difference Fourier peaks | Below ±0·4 e $Å^{-3}$ | Below ±0·2 e $Å^{-3}$ |

* Crystal was tetrahedral with 0·27 mm edges and height 0·25 mm from vertex to base.

For $NaZnNTA.H_2O$ all computations were performed on a Data General Eclipse S-250 computer with the *SHELXTL* (Sheldrick, 1981) suite of programs. For $Na_2HNTA$ all calculations were performed on a Data General Nova 1200 computer with the Syntex *XTL* programs.

## Discussion

Table 2. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* ($Å^2 \times 10^3$) *for* $NaZnNTA.H_2O$ *and* $Na_2HNTA$

The temperature-factor expression is $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.

| | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| $NaZnNTA.H_2O$ | | | | |
| Zn | −801 (2) | −3168 (1) | −1768 (1) | 10 (1)* |
| Na | 2037 (5) | −4429 (4) | −3600 (3) | 18 (1)* |
| N | −2622 (10) | −4431 (8) | −943 (7) | 8 (2) |
| O(1) | −838 (10) | −7407 (7) | −2145 (5) | 15 (2) |
| O(2) | −105 (9) | −5208 (7) | −2345 (6) | 14 (2) |
| O(3) | −2055 (9) | −1722 (7) | −760 (6) | 15 (2) |
| O(4) | −3832 (9) | −1496 (7) | 612 (6) | 14 (2) |
| O(5) | −2694 (9) | −3047 (8) | −2934 (5) | 20 (2) |
| O(6) | −5235 (12) | −3855 (9) | −3341 (8) | 41 (2) |
| O(7) | 2212 (10) | −3845 (8) | −5417 (6) | 22 (2) |
| C(1) | −876 (14) | −6147 (9) | −1868 (8) | 12 (2) |
| C(2) | −1915 (13) | −5823 (11) | −867 (9) | 13 (2) |
| C(3) | −2958 (13) | −2208 (9) | −27 (8) | 9 (2) |
| C(4) | −2883 (15) | −3763 (10) | 140 (9) | 14 (2) |
| C(5) | −4217 (14) | −4396 (10) | −1616 (9) | 20 (2) |
| C(6) | −4026 (16) | −3726 (11) | −2710 (10) | 25 (3) |
| H(2*a*) | −1191 | −5892 | −235 | 57 |
| H(2*b*) | −2821 | −6476 | −803 | 57 |
| H(4*a*) | −3928 | −4091 | 464 | 57 |
| H(4*b*) | −1955 | −3999 | 622 | 57 |
| H(5*a*) | −4596 | −5326 | −1713 | 57 |
| H(5*b*) | −5078 | −3906 | −1208 | 57 |
| $Na_2HNTA$ | | | | |
| Na(1) | 954 (2)† | $x$ | $x$ | 18 (1)* |
| Na(2) | 6132 (2)† | $x$ | $x$ | 21 (1)* |
| N | 1059 (5)† | $x$ | $x$ | 15 (1)* |
| C(1) | −1586 (7) | −2218 (6) | −117 (7) | 20 (2)* |
| C(2) | −479 (6) | −2503 (6) | 1066 (6) | 15 (2)* |
| O(1) | 355 (4) | −1527 (4) | 1348 (4) | 22 (1)* |
| O(2) | −577 (5) | −3682 (4) | 1656 (4) | 25 (1)* |
| H(N) | −428† | $x$ | $x$ | 50 |
| H(1*A*) | −1822 | −3133 | −595 | 50 |
| H(1*B*) | −2428 | −1770 | 372 | 50 |

* Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

† Atoms lie on a threefold axis with $x = y = z$.

Final atomic parameters are given in Table 2.* The structure of $NaZnNTA.H_2O$ is shown in Fig. 1. Bond lengths, bond angles, and torsion angles for the structure are given in Table 3. The structure is isomorphous with the $NaCuNTA.H_2O$ structure reported by Whitlow (1973). The structure consists of an intricate network of ligand-bridged coordination complexes with Na–O–Zn, Na–O–C–O–Zn and Zn–O–C–O–Zn linkages. The NTA ion functions as a tetradentate chelate coordinated to the $Zn^{2+}$ ion. The remaining two octahedral coordination sites are occupied by non-chelating O atoms from other $ZnNTA^-$ ions. The $Na^+$ ion links $ZnNTA^-$ ions by $\mu$-oxo bridges involving the atoms O(1), O(2) and O(3). Atom O(6) bonds the $Na^+$ ion to an adjacent $ZnNTA^-$ ion by an Na–O–C–O–Zn linkage. The O atom of the water molecule, O(7), is coordinated to the $Na^+$ ion. The coordination polyhedron about the $Na^+$ ion is intermediate between trigonal bipyramidal and square pyramidal.

Differences in the coordination preferences of $Ca^{2+}$ and $Zn^{2+}$ cations can be illustrated with a comparison of the $NaZnNTA.H_2O$ structure with those of $Ca_2EDTA.7H_2O$ (Barnett & Uchtman, 1979), $Zn_2EDTA.6H_2O$ (Pozhidaev, Polynova, Porai-Koshits & Neronov, 1973) and NaCaNTA (Barnett & Uchtman, 1979). The chelated $Ca^{2+}$ ion goes from an eight-coordinate, square-antiprismatic coordination in $Ca_2EDTA.7H_2O$ to a nitrogen-capped trigonal-antiprismatic coordination in NaCaNTA. A similar change in coordination environment is not observed for the $Zn^{2+}$ ions in $NaZnNTA.H_2O$ and

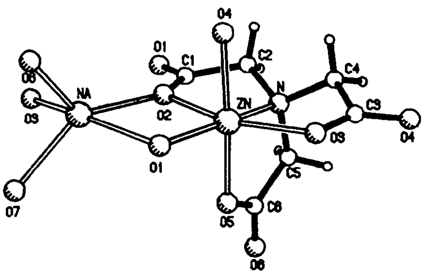

Fig. 1. Perspective drawing of the $NaZnNTA.H_2O$ complex.

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* Lists of structure factors, anisotropic thermal parameters, powder diffraction data for $Na_2HNTA$, $NaZnNTA.H_2O$, and NaCaNTA, and a description of the methods used to prepare the single-crystal samples have been deposited with the British Library Lending Division as Supplementary Publication No. SUP39019 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *for* NaZnNTA.$H_2O$ *and* $Na_2HNTA$

Cation coordination

| | | | |
|---|---|---|---|
| NaZnNTA.$H_2O$ | | | |
| Zn–O(1) | 2·001 (7) | Na–O(1) | 2·375 (8) |
| Zn–O(2) | 2·188 (6) | Na–O(2) | 2·410 (7) |
| Zn–O(3) | 2·124 (6) | Na–O(3) | 2·374 (8) |
| Zn–O(4) | 2·128 (6) | Na–O(6) | 2·242 (9) |
| Zn–O(5) | 2·071 (6) | Na–O(7) | 2·310 (8) |
| Zn–N | 2·146 (8) | | |
| O(1)–Zn–O(2) | 87·8 (3) | O(1)–Na–O(2) | 74·8 (3) |
| O(1)–Zn–O(3) | 116·2 (3) | O(1)–Na–O(3) | 156·3 (3) |
| O(1)–Zn–O(4) | 92·1 (3) | O(1)–Na–O(6) | 96·7 (3) |
| O(1)–Zn–O(5) | 88·8 (3) | O(1)–Na–O(7) | 101·0 (3) |
| O(1)–Zn–N | 163·7 (3) | O(2)–Na–O(3) | 85·3 (3) |
| O(2)–Zn–O(3) | 156·0 (3) | O(2)–Na–O(6) | 131·2 (4) |
| O(2)–Zn–O(4) | 83·9 (3) | O(2)–Na–O(7) | 137·7 (3) |
| O(2)–Zn–O(5) | 90·4 (3) | O(3)–Na–O(6) | 106·1 (3) |
| O(2)–Zn–N | 78·2 (3) | O(3)–Na–O(7) | 85·0 (3) |
| O(3)–Zn–O(4) | 93·0 (3) | O(6)–Na–O(7) | 91·0 (4) |
| O(3)–Zn–O(5) | 91·8 (3) | | |
| O(3)–Zn–N | 78·3 (3) | | |
| O(4)–Zn–O(5) | 174·2 (3) | | |
| O(4)–Zn–N | 94·7 (3) | | |
| O(5)–Zn–N | 83·1 (3) | | |
| $Na_2HNTA$ | | | |
| Na(1)–O(1) | 2·432 (5) | O(1)–Na(1)–O(1′) | 87·6 (2) |
| Na(1)–O(2) | 2·304 (4) | O(1)–Na(1)–O(2) | 175·1 (2) |
| Na(1)–N | 3·284 (8) | O(1)–Na(1)–O(2′) | 87·6 (2) |
| | | O(2)–Na(1)–O(2′) | 91·6 (2) |
| Na(2)–O(1) | 2·512 (4) | O(1)–Na(2)–O(1′) | 100·3 (1) |
| Na(2)–O(2) | 2·416 (5) | O(1)–Na(2)–O(2) | 173·7 (2) |
| | | O(1)–Na(2)–O(2′) | 84·0 (2) |
| | | O(2)–Na(2)–O(2′) | 91·9 (2) |

Glycinate-ring geometries*

| | $G_1$ | $G_2$ | $G_3$ | $G_{av}$ | $G$ |
|---|---|---|---|---|---|
| C–N | 1·47 (1) | 1·50 (1) | 1·50 (1) | 1·49 (2) | 1·492 (6) |
| C–C′ | 1·51 (1) | 1·54 (1) | 1·50 (1) | 1·52 (2) | 1·549 (8) |
| C–O | 1·25 (1) | 1·24 (1) | 1·27 (1) | 1·25 (2) | 1·238 (7) |
| C–O′ | 1·28 (1) | 1·25 (1) | 1·23 (1) | 1·26 (2) | 1·245 (7) |
| †*M*–O | 2·188 (6) | 2·124 (6) | 2·071 (6) | 2·13 (6) | 2·432 (5) |
| *M*–N | 2·146 (8) | | | | 3·284 (5) |
| N–C–C′ | 110·3 (8) | 108·6 (7) | 114·7 (8) | 111 (3) | 109·3 (5) |
| C–C′–O | 119·4 (9) | 117·0 (8) | 120·3 (9) | 119 (2) | 116·9 (5) |
| C–C′–O′ | 115·4 (8) | 119·1 (8) | 116·1 (11) | 117 (2) | 115·2 (5) |
| O–C–O′ | 125·1 (9) | 123·7 (9) | 123·6 (10) | 124 (1) | 127·9 (5) |
| *M*–N–C | 108·1 (6) | 105·1 (5) | 107·0 (5) | 107 (2) | 105·8 (4) |
| *M*–O–C′ | 113·4 (6) | 115·6 (6) | 114·4 (6) | 114 (1) | 145·9 (4) |
| O–*M*–N | 78·2 (3) | 78·3 (3) | 83·1 (3) | 80 (3) | 53·1 (10) |
| *M*–N–C–C′ | −34·9 (9) | 41·0 (9) | 9·5 (10) | | −29·2 (4) |
| N–C–C′–O | 31·4 (13) | −33·9 (13) | −11·7 (4) | | 22·7 (7) |
| C–C′–O–*M* | −10·2 (12) | 7·0 (11) | 7·1 (13) | | 8·5 (10) |
| C′–O–*M*–N | −8·1 (7) | 13·8 (7) | −0·9 (7) | | −19·9 (9) |
| O–*M*–N–C | 23·6 (6) | −29·8 (6) | −4·8 (6) | | 23·1 (8) |

* Atom labeling scheme for the glycinate rings is shown in Fig. 1. $G_1$ contains C(2), $G_2$ contains C(4), and $G_3$ contains C(5). $G$ is the glycinate ring in $Na_2HNTA$.

† *M* represents the metal ion: Zn in NaZnNTA.$H_2O$ and Na(1) in $Na_2HNTA$.

$Zn_2EDTA.6H_2O$. In both $Zn^{2+}$ structures the metal-ion coordination is distorted octahedral.

Comparison of molecular models for NaCaNTA and NaZnNTA.$H_2O$ reveals significant differences in the stereochemistries of the coordinated NTA ligands. To compare these structures quantitatively one must consider four features of the geometry of the coordinated NTA ligands: (i) the *M*–N bond length, (ii) the O–*M*–O bond angles, (iii) the average C–O–*M* bond angle and (iv) the geometries of the five-atom chelate rings. The Zn–N bond length, 2·146 (8) Å, is significantly shorter than the Ca–N bond length, 2·629 (2) Å, in NaCaNTA. The O(2)–Zn–O(3) bond angle, 156·0 (3)°, is closer to linear than the related O(2)–Ca–O(2) bond angles, 103·8 (1)°. The average Zn–O–C bond angle, 114 (1)°, is significantly smaller than the Ca–O–C bond angle, 126·0 (4)°. The array of chelate-ring conformations is quite different for the two structures. The chelate rings of NaCaNTA are related by a crystallographic threefold axis of symmetry which requires that they adopt identical conformations.

The geometries of the chelate rings can be described by the endocyclic torsion angles of the glycinate residues given in Table 4. The data in this table indicate a common feature for all published structures of octahedral transition-metal complexes containing a tetradentate NTA ion. Each structure reveals two five-atom rings in envelope conformations related by a pseudo-mirror plane defined by the third (flat) ring. Thus, the torsion angle $\omega_1$ in ring (2) is approximately equal in magnitude to $\omega_1$ of ring (3) but of opposite sign. A similar relationship holds for the other four torsion angles. The torsion angles in ring (1) are nearly zero and are consistent with a flat ring. The resultant 'butterfly' structure is shown in Fig. 2.

The tetradentate NTA ion assumes different conformations in LiCuNTA.$3H_2O$ (Fomenko, Kopaneva, Porai-Koshits & Polynova, 1974), $Na_3NTA.H_2O$ (Daly, 1967), and in NaCaNTA (Barnett & Uchtman, 1979). The three chelate rings in LiCuNTA.$3H_2O$ assume envelope conformations to accommodate the square-pyramidally coordinated $Cu^{2+}$ ion. The chelate rings in NaCaNTA assume half-chair conformations to allow the $Ca^{2+}$ ion to assume a monocapped trigonal-antiprismatic coordination geometry. The geometries of the chelate rings in $Na_3NTA.H_2O$ are discussed below.

The solid-state structure of $Na_2HNTA$ can be considered as the $Na^+$ salt of $NaHNTA^-$ and is illustrated in Fig. 3. Bond lengths and bond angles for the structure are given in Table 3. This structure is very similar to the crystal structure of NaCaNTA (Barnett & Uchtman, 1979). Although the two structures are not isomorphous (as shown by powder diffraction analyses), both utilize the crystallographic symmetry of the cubic space group $P2_13$ in a similar manner.

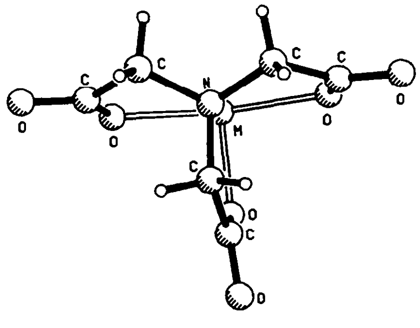
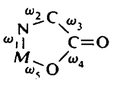


Fig. 2. Perspective drawing to illustrate the 'butterfly' conformation characteristic of tetradentate NTA ligands.

Table 4. *Endocyclic torsion angles* (°) *for tetradentate NTA complexes*



| | $NaZnNTA.H_2O$[(a)] | $LiCuNTA.3H_2O$[(b)] | $Cs_4[TiO(NTA)]_4.6H_2O$[(c)] | | | | $KCoNTA.3H_2O$[(d)] | $KCuNTA.3H_2O$[(e)] |
|---|---|---|---|---|---|---|---|---|
| | | | Ti(1) | Ti(2) | Ti(3) | Ti(4) | | |
| Ring (1) | | | | | | | | |
| $\omega_1$ | −4·8 | 12·1 | −4·4 | −2·1 | 0·7 | 5·2 | 6·4 | −8·3 |
| $\omega_2$ | 9·5 | −29·9 | 2·4 | 0·5 | −6·9 | −3·5 | −13·0 | 13·7 |
| $\omega_3$ | −11·7 | 38·6 | 2·7 | 2·7 | 13·2 | −1·6 | 16·3 | −16·7 |
| $\omega_4$ | 7·1 | −25·1 | −7·4 | −5·3 | −13·7 | 7·3 | −10·0 | −9·6 |
| $\omega_5$ | −0·9 | 7·9 | 6·5 | 4·3 | 7·0 | −7·1 | 2·0 | 0·0 |
| Ring (2) | | | | | | | | |
| $\omega_1$ | 23·6 | 26·1 | 27·3 | 24·9 | 28·0 | 34·7 | 25·7 | 25·1 |
| $\omega_2$ | −34·9 | −27·4 | −30·0 | −28·1 | −29·3 | −38·5 | −25·0 | −34·8 |
| $\omega_3$ | 31·4 | 17·6 | 18·9 | 18·8 | 15·6 | 23·0 | 6·9 | 25·1 |
| $\omega_4$ | −10·2 | 3·2 | 6·1 | 4·7 | 12·1 | 9·4 | 16·9 | −3·1 |
| $\omega_5$ | −8·1 | −15·6 | −18·8 | −16·8 | −22·9 | −25·0 | −24·5 | −12·6 |
| Ring (3) | | | | | | | | |
| $\omega_1$ | −29·8 | −19·7 | −31·1 | −30·2 | −30·2 | −25·3 | −23·5 | −35·3 |
| $\omega_2$ | 41·0 | 25·0 | 36·9 | 30·1 | 29·2 | 27·6 | 31·4 | 36·7 |
| $\omega_3$ | −33·9 | −20·0 | −25·7 | −14·0 | −11·1 | −14·4 | −24·2 | −8·1 |
| $\omega_4$ | 7·0 | 2·3 | −3·6 | −16·0 | −19·4 | −11·1 | 2·5 | −20·8 |
| $\omega_5$ | 13·8 | 9·9 | 20·0 | 26·1 | 28·1 | 21·4 | 12·4 | 31·8 |

References: (*a*) This work. (*b*) Fomenko, Kopaneva, Porai-Koshits & Polynova (1974). (*c*) Wieghardt, Quiltzsch, Weiss & Nuber (1980). (*d*) Battaglia, Corradi & Tani (1975). (*e*) Fomenko, Polynova & Porai-Koshits (1975*a*, *b*).

In both structures the chelated complex has a threefold axis of symmetry passing through the N atom and the chelated metal ion. Both crystal structures have formed an intricate, anhydrous network of NTA-chelated complexes linked together by O-bridging $Na^+$ ions and by non-chelating O atoms which fill out the coordination spheres of the cations. No discrete complexes exist.

In contrast to the NaCaNTA complex, the NTA ligand is a zwitterion in $Na_2HNTA$ and functions as a tridentate ligand to the $Na^+$ ion. The N atom is unavailable as a donor site. Because the N atom is protonated in $Na_2HNTA$, as shown in Fig. 3, the Na(1)–N distance is (0·51 Å) longer than the Ca–N distance in NaCaNTA. A graphical comparison of the $CaNTA^-$ and $NaHNTA^-$ anions is presented in Fig. 4 which illustrates a least-squares superposition of the NTA ligands and metal atoms of the two anions. This displacement also manifests itself in a difference in the coordination geometries of the chelated metal atoms, but not just a simple difference in coordination number. Na(1) is in a nearly ideally octahedral coordination rather than a trigonal-antiprismatic coordination, which would result if the differences were a simple removal of the N site from the capped trigonal-antiprismatic coordination about Ca in NaCaNTA. The coordination environment of Na(2) is also nearly ideally octahedral and is provided by six O atoms from six symmetry-related $NaHNTA^-$ ligands.

A comparison between the zwitterions in $Na_2HNTA$ and $H_3NTA$ (Stanford, 1967) is not informative because the triprotic acid is not in a conformation suitable for tridentate coordination. Using the four geometrical features [(i)–(iv)] of the NTA ligand mentioned above, a better comparison can be made between $Na_2HNTA$ and $Na_3NTA.H_2O$ (Daly, 1967). The simplest features [(i) and (iii)] for comparison are the *M*–N distances (3·284 and 2·449 Å respectively) and the C–O–*M* angles (145·9 and 116·2° respectively). These two features show the flexibility of the NTA ion in chelating $Na^+$ ions, even though the N atom is protonated in the $NaHNTA^-$ ion and cannot coordinate to the $Na^+$ ion. Because the coordination geometries about the chelated $Na^+$ ions are sufficiently different, the O–*M*–O angles (ii) are not comparable.

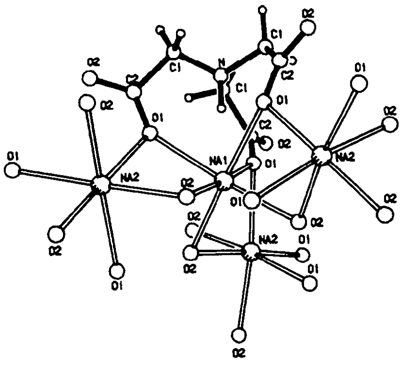


Fig. 3. Perspective drawing of the $Na_2HNTA$ complex.

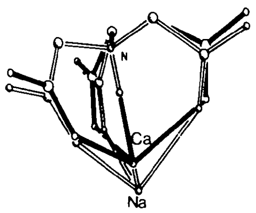


Fig. 4. Perspective drawing comparing the $CaNTA^-$ and $NaHNTA^-$ anions.

Table 5. *Torsion angles* (°) *of the glycinate rings in* $Na_3NTA.H_2O$

Atom labeling scheme for the glycinate residues is taken from Daly (1967). The coordinates were obtained from the Cambridge Crystallographic Database. $G_1$ contains C(1), C(2), O(1); $G_2$ contains C(3), C(4), O(4); and $G_3$ contains C(5), C(6), O(5).

| | $G_1$ | $G_2$ | $G_3$ |
|---|---|---|---|
| Na(1)–N–C–C′ | −32·5 | −16·8 | −46·5 |
| N–C–C′–O | 37·3 | 45·4 | 44·4 |
| C–C′–O–Na(1) | 19·8 | −49·0 | −16·9 |
| C′–O–Na(1)–N | 1·1 | 28·4 | −6·6 |
| O–Na(1)–N–C | 17·8 | −2·9 | 28·2 |

Differences in the torsion angles of the glycinate rings (see Table 5) of the two structures also illustrate the ligand's flexibility. In $NaHNTA^-$ the conformations of the glycinate rings are identical by symmetry. As would be expected from the large C–O–*M* angle, the absolute values for the torsion angles are smaller in $Na_2HNTA$ than in $Na_3NTA.H_2O$. The conformations of the glycinate rings in $Na_3NTA.H_2O$ are not constrained by symmetry. For two of the rings, $G_1$ and $G_3$, the torsion angles are nearly identical in sign and magnitude. These two glycinate rings are in envelope conformations with the $sp^3$-hybridized C atom residing out of the plane of the other four atoms. In the third glycinate ring the $sp^2$-hybridized C atom is out of the plane and also contains the smallest of the three *M*–O–C angles (112·8°).

The crystal structure of $Na_2HNTA$ is more compact than that of the related trisodium NTA salt (Daly, 1967). This feature may account for the monohydrated form of $Na_3NTA$ and the anhydrous form of $Na_2HNTA$.

## X-ray powder diffraction data

The X-ray powder patterns of $NaZnNTA.H_2O$, $Na_2HNTA$ and NaCaNTA were collected to facilitate the identification of polycrystalline samples of the compounds.* The data for $Na_2HNTA$ and NaCaNTA clearly showed the structures are not isomorphous. A least-squares refinement of the indexed powder diffraction lines resulted in the lattice parameter $a$ = 9·6217 (7) Å for NaCaNTA and the lattice parameters $a$ = 7·919 (3), $b$ = 9·759 (2) and $c$ = 12·291 (6) Å for $NaZnNTA.H_2O$. The values are in good agreement with the values from the single-crystal measurements.

For $Na_2HNTA$ the sample from which the single crystal was obtained for the structure study was not available. The pattern was calculated from the single-crystal structure parameters using the *POWD*10 program of Smith & Nichols (1981).

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* JCPDS Diffraction File Nos. 34-1983, 34-1981 and 34-1982, respectively. See also deposition footnote.