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Structure of Sodium Nitrilotriacetatocopper(II) Monohydrate

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The crystal and molecular structure of sodium nitrilotriacetatocopper(II) monohydrate, $NaCuN(CH_2COO)_3 \cdot H_2O$, has been determined by single-crystal X-ray analysis. The compound is formed when Cu^{2+} ions are leached from copper tubing by an aqueous solution of $Na_3N(CH_2COO)_3$. The crystals are orthorhombic, with $a = 9.899$ (5), $b = 12.565$ (5), and $c = 7.548$ (5) Å, and belong to the space group $P2_12_12_1$. There are four formula units in the unit cell. The atomic coordinates and anisotropic thermal parameters have been refined by full-matrix least-squares methods from diffractometer data to a final R value of 0.032 for 947 independent observed reflections. Each copper atom in the structure is effectively chelated by an enveloping nitrilotriacetate (NTA) group by means of four connecting bonds (three O-Cu, one N-Cu). Additional contacts between neighboring NTA groups and the copper complete a distorted octahedral coordination which is nevertheless characterized by the usual two long-four short arrangement of bonds. The Cu-O bond lengths range between 1.950 (4) and 2.351 (4) Å. The sodium atoms are bonded to four adjacent NTA groups and a water molecule with Na-O distances from 2.282 (5) to 2.372 (5) Å. Evidence for a 1:2 Cu-NTA complex and speculation about the Cu-NTA structure in solution are presented.

Introduction

For ecological reasons limits have recently been imposed on the maximum phosphate content of detergents. These restrictions have prompted the use of other solubilizing agents, the best known (and most controversial) of which is the trisodium salt of nitrilotriacetic acid (Na_3NTA). Considerable research has been carried out on nitrilotriacetic acid (H_3NTA) and its derivatives including several crystallographic studies: $K_2Zr(NTA)_2 \cdot H_2O$,[1] H_3NTA,[2] $Na_3NTA \cdot H_2O$,[3] and $CaHNTA \cdot 2H_2O$.[4] In addition, preliminary reports have appeared for $LiCuNTA \cdot 3H_2O$[5] and $K_4Ni(NTA)_2 \cdot 8H_2O$.[6] In general, these investigations have shown the NTA group to be multidentate, but shared among several cations in the crystal structure. In $CaHNTA \cdot 2H_2O$, for example, although five Ca-NTA bonds exist, only one bond is formed between an NTA group and a particular calcium atom. A test in our laboratory, however, has suggested that the interaction between Cu^{2+} and the NTA^{3-} ion could be considerably stronger and more specific.

In our experiment, an aqueous solution of 0.1 *M* Na_3NTA (pH ~11) was circulated continuously through a coil of copper tubing. During a period of several days the initially colorless solution became blue suggesting a complex had been formed between the NTA group and copper ions leached from the inside of the tubing walls. This effect is somewhat alarming since much modern plumbing is made of copper and could conceivably be damaged by the presence of NTA in washing solutions. The present X-ray analysis was undertaken to investigate the chemical structure of the complex formed.

Experimental Section

When an aqueous solution of H_3NTA and $Cu(NO_3)_2$ (made basic with Na_2CO_3) is evaporated to dryness, crystals of sodium nitrilotriacetatocopper(II) monohydrate, $NaCuN(CH_2COO)_3 \cdot H_2O$ (hereafter $NaCuNTA \cdot H_2O$), precipitate as pale blue prisms. Infrared spectra and X-ray powder patterns confirm that these are identical with crystals formed from solutions obtained by passing aqueous Na_3NTA through copper pipes. The crystals precipitate together with a darker polycrystalline form which is thought to be a 1:2 Cu-NTA complex from atomic absorption analysis (for Na and Cu) and preliminary X-ray work.

$Cu(H_2NTA)_2 \cdot 2H_2O$. X-Ray investigation of this dark blue compound was limited to a photographic determination of the unit cell parameters and space group. The cell constants determined are $a = 6.86$ (3), $b = 14.05$ (3), $c = 9.42$ (3) Å, and $\beta = 91° \; 45 \; (10)'$, with the monoclinic space group $P2_1/c$ ($C_{2h}{}^5$) indicated by the systematic absences $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$. The density measured by flotation, 1.72 (2) g cm^{-3}, and the unit cell dimensions suggest the tentative formula $Cu(H_2NTA)_2 \cdot 2H_2O$. For this formula the calculated density is 1.76 g cm^{-3} assuming two formula units per unit cell.[7]

$NaCuNTA \cdot H_2O$. The remainder of the paper refers to the pale blue $NaCuNTA \cdot H_2O$ compound for which a complete structure determination has been carried out. The crystal selected for the X-ray measurements was mounted on an arcless goniometer head with a approximately parallel to the ϕ axis of the diffractometer. The {011} faces were prominent and the crystal measured 0.17 × 0.13 mm in the [011] and [01$\bar{1}$] directions, respectively. The overall length was 0.26 mm with the top capped by four faces. The unit cell parameters were derived by a least-squares technique from the optimum settings of 22 reflections aligned on an automatic four-circle diffractometer using a takeoff angle of 1.5° and a graphite monochromator with Mo $K\alpha_1$ radiation (λ 0.70926 Å). The cell dimensions were determined to be $a = 9.899$ (5), $b = 12.565$ (5), and $c = 7.548$ (5) Å at 22°. The crystal is orthorhombic and belongs to the space group $P2_12_12_1$

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[3] J. J. Daly, *J. Chem. Soc. A*, 1708 (1967).

[4] S. H. Whitlow, *Acta Crystallogr., Sect. B*, 28, 1914 (1972).

[5] V. V. Fomenko, L. I. Kopaneva, T. N. Polynova, M. A. Porai-Koshits, N. D. Mitrofanova, and L. I Marmynenko, *Zh. Strukt. Khim.*, 13, 166 (1972).

[6] V. V. Fomenko, T. N. Polynova, M. A. Porai-Koshits, and N. D. Mitrofanova, *Zh. Strukt. Khim.*, 13, 343 (1972).

[7] Some structural deductions about this compound can be made because the presence of only two formula units in the unit cell would position the Cu atoms at crystallographic centers of symmetry. This would allow a maximum of three bonds between copper and each NTA group for the coordination number not to exceed 6. Peaks at 1695 and 1725 cm^{-1} in the infrared spectrum of the solid (measured in Nujol) can be assigned to uncoordinated -COOH stretching vibrations and suggest that two carboxylate groups are not bonded directly to the metal atom. The remaining Cu-N and Cu-O bonds between Cu and each NTA group must be arranged so as to preserve centrosymmetry, and two water molecules probably bond to Cu to complete an octahedral configuration.

Table I. Final Positional Coordinates and Anisotropic Thermal Parameters[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	3098 (1)	1806 (1)	704 (1)	18.3 (3)	13.6 (3)	13.9 (3)	1.4 (4)	−2.0 (4)	0.9 (4)
Na	−623 (2)	1373 (2)	2076 (3)	23 (1)	26 (1)	21 (2)	4 (1)	3 (1)	2 (1)
N	4271 (5)	1023 (4)	2593 (7)	15 (2)	13 (2)	15 (3)	−1 (2)	0 (3)	4 (2)
C(1)	5704 (6)	960 (5)	1981 (8)	15 (3)	22 (3)	19 (3)	−3 (3)	−1 (3)	8 (3)
C(2)	6119 (6)	1957 (5)	975 (8)	34 (4)	11 (3)	11 (3)	−3 (3)	1 (3)	2 (3)
C(3)	3714 (6)	−47 (5)	2957 (9)	23 (3)	18 (3)	21 (3)	−2 (3)	3 (3)	6 (3)
C(4)	2167 (6)	19 (5)	3093 (8)	25 (4)	20 (3)	11 (3)	0 (4)	0 (3)	−1 (3)
C(5)	4203 (6)	1701 (5)	4210 (8)	29 (3)	24 (3)	21 (3)	0 (3)	1 (3)	0 (4)
C(6)	3628 (7)	2808 (5)	3859 (8)	43 (4)	20 (3)	20 (4)	0 (3)	3 (3)	0 (3)
O(1)	5275 (4)	2449 (3)	72 (6)	13 (2)	24 (2)	32 (2)	−3 (2)	−5 (2)	10 (2)
O(2)	7371 (4)	2209 (3)	1067 (6)	14 (2)	25 (2)	22 (3)	−2 (2)	0 (2)	8 (2)
O(3)	1611 (4)	769 (3)	2279 (6)	20 (3)	28 (2)	31 (3)	1 (2)	2 (2)	13 (3)
O(4)	1544 (4)	−681 (3)	3910 (5)	22 (3)	22 (2)	24 (3)	−3 (2)	2 (2)	11 (2)
O(5)	2964 (5)	2948 (3)	2445 (5)	38 (3)	20 (2)	20 (2)	14 (2)	−12 (2)	−6 (2)
O(6)	3797 (6)	3490 (3)	5007 (6)	91 (4)	28 (3)	24 (2)	7 (3)	−14 (3)	−12 (2)
O(W)	−1076 (5)	−413 (4)	2101 (6)	57 (3)	26 (3)	50 (4)	−11 (3)	9 (3)	−2 (3)

[a] The coordinates are given ×10^4, the vibrational parameters are ×10^3, and the esd's are given in terms of the least significant digit. The temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^* \cos \alpha^*]$.

($D_2{}^4$) on the basis of the systematic absences $h00$, $h \neq 2n$, $0k0$, $k \neq 2n$, and $00l$, $l \neq 2n$. The density calculated for one formula weight per asymmetric unit, 2.07 g cm^{-3}, agrees well with the density measured by flotation, 2.05 (2) g cm^{-3}.

A total of 983 independent reflections having $2\theta \leqslant 50°$ were measured by the θ–2θ scan technique using Mo Kα radiation with a take-off angle of 5°. The scan speed was 2°/min and the scan range was adjusted for the crystal mosaicity and the wavelength dispersion. The function $1.7 + 0.69 \tan \theta$ was used to determine the scan width for each reflection. Fifteen-second background measurements were made either side of each scan and three standard reflections (490, 182, 206) were remeasured after every 25 reflections for checking and scaling purposes. There was no appreciable decomposition of the crystal and repeated measurements of the intensities of the standard reflections varied <5%. Lorentz and polarization factors were applied and weights were assigned to the intensities on the basis of counting statistics and instrument stability.[8] Where the net intensity for a reflection was $<1.65\sigma(I)$, where $\sigma(I)$ is the associated standard deviation, the reflection was classified unobserved. At this significance level 36 reflections were considered to be unobserved and were assigned threshold values equal to $1.65\sigma(I)$. Absorption corrections ($\mu = 24.87$ cm^{-1}) were calculated by the gaussian quadrature method. For these, the crystal was measured on the diffractometer and was described by eight well-defined faces and a flat base. The calculated transmission factors varied between 0.634 and 0.761. No extinction correction was applied.

Solution and Refinement of the Structure. The structure was solved using the heavy-atom technique and refined by full-matrix least-squares methods; the majority of the calculations including the absorption corrections were done using the X-RAY system of programs.[9] Neutral atomic scattering factors were used for all atoms[10] and for Cu the real and imaginary components of anomalous dispersion were included.[11] The quantity minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$ where the weight, w, is equal to $1/\sigma^2(F_o)$;[8] $|F_o|$ and $|F_c|$ are the amplitudes of the observed and calculated structure factors. The unobserved reflections were not used in the least-squares refinement which was begun using data uncorrected for absorption. The nonhydrogen atom positions were refined with isotropic temperature parameters to an R value ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.061 and with anisotropic parameters to $R = 0.044$. The hydrogen atom positions were located at peaks of 0.3–0.7 e Å^{-3} on a difference Fourier summation and were included in subsequent structure factor calculations with isotropic temperature factors ($B = 4.0$ Å^2) but were not refined. The H positions were all chemically reasonable and were between 0.93 and 1.16 Å from the appropriate C or O atom. At this stage the absorption-corrected data were used for two final cycles of least-squares refinement. None of the atomic coordinates changed by $>2\sigma$ although some of the thermal parameters varied by as much as 8σ. The final agreement factor is 0.032 and the weighted R factor ($R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$) is also 0.032 for the 947 observed reflections.[12] There are 6.7 observations for each parameter refined and in the last least-squares cycle the maximum shift to error ratio was 0.3; the mean, 0.06. The greatest fluctuation on the final difference map (−0.8 e Å^{-3}) occurred near the Cu position; there were no other peaks >0.4 e Å^{-3}. The refined positional and thermal parameters are in Table I, and the hydrogen atom coordinates are given in Table II.

Table II. Hydrogen Atom Coordinates[a]

Atom	x	y	z
H(C1)	572	50	96
H(C2)	640	92	322
H(C3)	400	−55	196
H(C4)	400	−39	417
H(C5)	520	176	465
H(C6)	340	145	496
H(W1)	−164	−95	252
H(W2)	−128	−16	87

[a] The coordinates given ×10^3 were not refined.

Results and Discussion

The stability of the complex formed between NTA and Cu is evident from the high degree of chelation. Four different chemical bonds, one from each carboxylate group and one from the central nitrogen atom, hold each copper atom to an enveloping NTA group (Figure 1). In this way, the Cu atom is held by three five-membered rings (or equivalently three eight-membered rings). The arrangement is somewhat similar to the geometry about one of the sodium atoms (Na(1)) in $Na_3NTA \cdot H_2O$ but is markedly different from the coordination about calcium in $CaHNTA \cdot 2H_2O$ where there is only one bond between NTA and each neighboring calcium atom. The added strength of the Cu-NTA complex is due, in part, to the metal-nitrogen bond which is not formed in the calcium case.

NTA Structure and Conformation. The internal geometry of the NTA group is constrained to accommodate the Cu atom, but some chemical inference can be drawn from variations in the carbon-oxygen bond lengths (Table III) and from the relationship of the carboxylate groups to the copper atom. The shortest C–O bond length, C(6)–O(6), of 1.231 (8) Å involves the only oxygen atom not bonded to a copper atom and presumably contains considerable double-bond character. The lack of a bond between O(6) and cop-

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(12) See paragraph at end of paper regarding supplementary material.

Table III. Bond Lengths (Å) and Angles (deg)^a

	Nitrilotriacetate Group		
N-C(1)	1.494 (8)	C(1)-N-C(3)	111.3 (5)
N-C(3)	1.479 (8)	C(1)-N-C(5)	109.1 (5)
N-C(5)	1.490 (8)	C(3)-N-C(5)	110.5 (5)
C(1)-C(2)	1.521 (9)	N-C(1)-C(2)	111.6 (5)
C(3)-C(4)	1.538 (8)	N-C(3)-C(4)	109.6 (5)
C(5)-C(6)	1.526 (9)	N-C(5)-C(6)	113.3 (5)
		C(1)-C(2)-O(1)	120.1 (5)
O(1)-C(2)	1.242 (7)	C(1)-C(2)-O(2)	116.0 (5)
O(2)-C(2)	1.281 (7)	O(1)-C(2)-O(2)	123.9 (5)
O(3)-C(4)	1.252 (8)	C(3)-C(4)-O(3)	116.5 (5)
O(4)-C(4)	1.239 (8)	C(3)-C(4)-O(4)	119.4 (6)
O(5)-C(6)	1.266 (8)	O(3)-C(4)-O(4)	124.0 (5)
O(6)-C(6)	1.231 (8)	C(5)-C(6)-O(5)	117.9 (5)
		C(5)-C(6)-O(6)	117.5 (6)
		O(5)-C(6)-O(6)	124.5 (6)
	Copper Coordination		
Cu-N	2.086 (5)	O(1)-Cu-O(3)	152.5 (2)
Cu-O(1)	2.351 (4)	O(1)-Cu-O(5)	86.9 (2)
Cu-O(3)	2.297 (4)	O(1)-Cu-O(4)^b	86.7 (2)
Cu-O(5)	1.950 (4)	O(1)-Cu-O(2)^c	88.9 (2)
Cu-O(4)^b	1.989 (4)	O(3)-Cu-O(5)	91.4 (2)
Cu-O(2)^c	1.958 (4)	O(3)-Cu-O(4)^b	93.6 (2)
N-Cu-O(1)	77.9 (2)	O(3)-Cu-O(2)^c	118.5 (2)
N-Cu-O(3)	74.7 (2)	O(5)-Cu-O(4)^b	173.5 (2)
N-Cu-O(5)	85.6 (2)	O(5)-Cu-O(2)^c	88.3 (2)
N-Cu-O(4)^b	91.8 (2)		
N-Cu-O(2)^c	165.7 (2)	O(4)^b-Cu-O(2)^c	92.9 (2)
	Sodium Coordination		
Na-O(3)	2.344 (5)	O(1)^c-Na-O(W)	133.8 (2)
Na-O(1)^c	2.369 (5)	O(1)^c-Na-O(2)^d	79.5 (2)
Na-O(W)	2.288 (5)	O(1)^c-Na-O(6)^e	135.1 (2)
Na-O(2)^d	2.372 (5)	O(W)-Na-O(2)^d	105.8 (2)
Na-O(6)^e	2.282 (5)	O(W)-Na-O(6)^e	90.9 (2)
O(3)-Na-O(1)^c	83.8 (2)	O(2)^d-Na-O(6)^e	93.8 (2)
O(3)-Na-O(W)	82.3 (2)		
O(3)-Na-O(2)^d	162.6 (2)		
O(3)-Na-O(6)^e	101.5 (2)		

^{a} Estimated standard deviations in the last figures are given in parentheses. ^{b} $-x + 1/2, -y, z - 1/2$. ^{c} $x - 1/2, -y + 1/2, -z$. ^{d} $x - 1, y, z$. ^{e} $x - 1/2, -y + 1/2, -z + 1$.

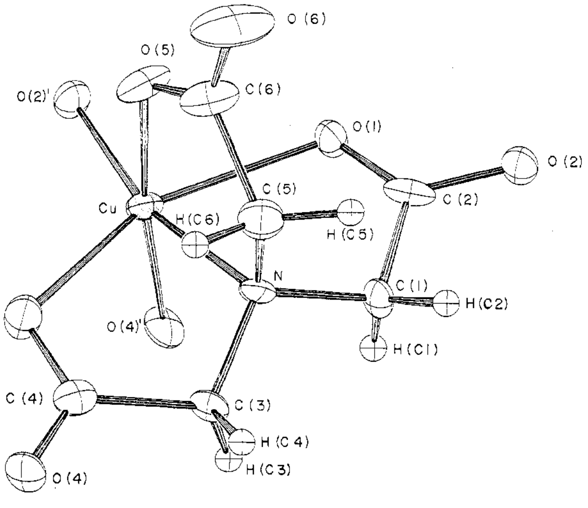

Figure 1. Structure of the Cu-NTA chelate. The ellipsoids represent 50% probability and the atoms designated by primes are in symmetry-related molecules.

per probably also accounts for the high thermal vibration of this atom. The longest C-O bond lengths in the NTA group are O(2)-C(2) and O(5)-C(6), 1.281 (7) and 1.266 (8) Å, respectively. These weaker C-O bonds are correlated with relatively strong Cu-O interactions since the shortest Cu-O bond lengths involve the oxygen atoms O(2) and O(5).

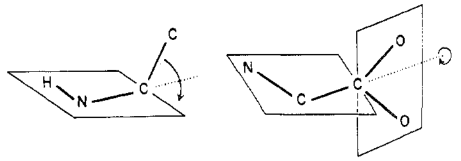

Figure 2. Torsion angles in each arm of the NTA molecule.

Table IV. Torsion Angles (deg) in NTA Structures

(C-C)-(N-H)^a			Compd	COO-CCN^b			|Av|^c
24.9	−174.4	37.3	H_3NTA[2]	1.9	4.9	13.3	6.7
−33.6	−22.9	−38.3	$Na_3NTA \cdot 2H_2O$[3]	33.2	40.5	39.2	37.6
−40.4	39.9	−42.0	$CaHNTA \cdot 2H_2O$[4]	−27.7	3.2	13.8	14.9
39.0	−45.8	12.9	$NaCuNTA \cdot H_2O$	−30.9	24.3	16.7	24.0

^{a} Defined as the angle, measured counterclockwise, that the projection of bond C-C makes with the reference bond N-H (H position real or hypothetical) when viewed in the direction C→N. ^{b} Defined as the acute angle that the COO plane makes with the reference CCN plane when viewed in the direction $O_2C \rightarrow C$, a counterclockwise rotation of the COO plane being positive. ^{c} The average of the magnitudes of the COO-CCN angles.

The conformation of the NTA entity is variable and different shapes are found in different environments. Although the bond lengths and valency angles are similar in different compounds, the "arms" of the group are free to take up optimum positions. To describe these different conformations it is convenient to refer to torsion angles at the two carbon atoms in each arm of the NTA molecule. These angles are illustrated in Figure 2, where the positive sense of each angle is indicated by an arrow, and are given in Table IV for different NTA structures. In $Na_3NTA \cdot 2H_2O$ and $NaCuNTA \cdot H_2O$ where there is no H atom bonded to N a hypothetical position has been calculated to define the torsion angle.

The (C-C)-(N-H) dihedral angles describe the direction in which the individual C-C bonds point. The angles indicate that in H_3NTA two arms point upward toward the hydrogen position but the third is directed downward. This arrangement permits all three arms of the NTA group to be involved in the extensive hydrogen-bonded network present in this structure. In the other compounds, however, the normal conformation is one with all three arms pointing upward in varying degrees. From a steric viewpoint such an arrangement is favorable because pointing the C-C bonds upward toward the H position also directs the arms outward and eliminates close oxygen-oxygen contacts. The tendency of the NTA molecule to have all three arms directed toward the H position is not due to intramolecular hydrogen bonding since in $Na_3NTA \cdot H_2O$ and $NaCuNTA \cdot H_2O$, the hydrogen atom on nitrogen is only hypothetical. In $NaCuNTA \cdot H_2O$, however, this orientation does permit strong chelation of the Cu atom and the arm (C(5)C(6)O(5)O(6)) which forms the axial bond to Cu has the smallest dihedral angle, 12.9°. The angle each carboxyl group makes with its respective arm is also useful in characterizing the NTA conformation. In H_3NTA the COO and CCN planes remain approximately parallel (average angle 6.7°) but as the NTA group becomes more involved with metal atoms, the carboxyl groups become progressively more twisted. Therefore in $CaHNTA \cdot 2H_2O$ the average angle is 14.9° but in $NaCuNTA \cdot H_2O$ where the NTA is multiply bonded to a single metal, it is 24.0°. The large torsion angle, 37.6°, for $Na_3NTA \cdot H_2O$ is a result of each NTA group being subjected to a large array of intermolecular contacts involving some 15 Na-O bonds.

Copper Environment. The copper coordination is shown[13] in Figures 1 and 3, and the appropriate bond lengths and

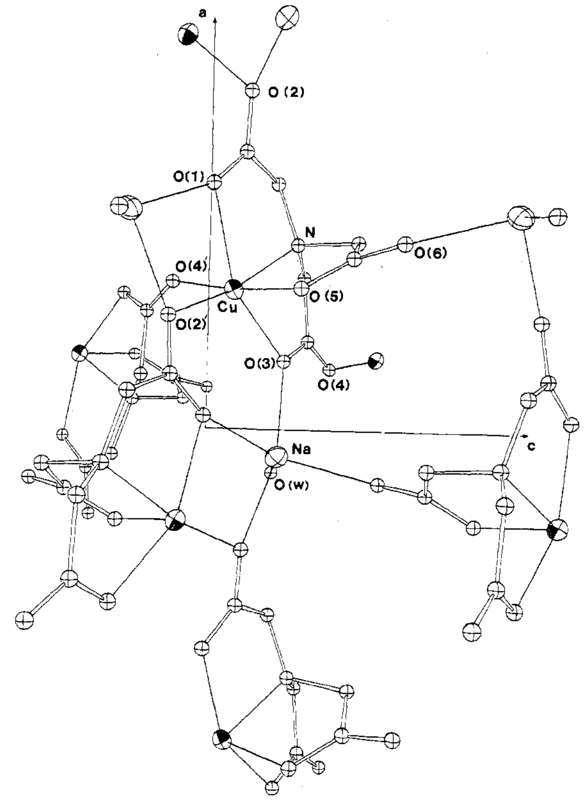

Figure 3. A perspective view of the packing in NaCuNTA·H_2O. The view, looking down the *b* axis, selectively shows the basic NTA structure, the metal atoms to which it bonds, and complete Cu and Na coordinations.

angles are given in Table III. Of the four contacts with the adjacent NTA molecule, O(1) and O(3) occupy axial positions in the distorted octahedral coordination while N and O(5) have equatorial positions. The octahedron is distorted because of the NTA chelation. In particular, the O(1)-Cu-O(3) angle is only 152.5° instead of the ideal 180°. Contacts with O(2)′ at $x - \frac{1}{2}, -y + \frac{1}{2}, -z$ and O(4)′ at $-x + \frac{1}{2}, -y, z - \frac{1}{2}$ complete the equatorial plane of the octahedron and provide links to two neighboring NTA groups. The least-squares plane through the four equatorially located atoms is $0.874X + 0.402Y - 0.272Z = 3.618$, where the coefficients are direction cosines relative to the crystallographic axes. The four atoms are planar (maximum deviation 0.07 Å), the copper atom is only slightly displaced toward O(3) (0.17 Å), and O(1) and O(3) are located 2.17 and 2.30 Å above and below the plane. This arrangement of two longer axial bonds (average 2.324 Å) and four shorter equatorial bonds (average 1.996 Å including the Cu-N bond) is common in copper complexes and these distances are not remarkable.

Sodium Environment. The sodium ions are surrounded by five oxygen atoms in a very distorted trigonal-bipyramidal arrangement (Table III and Figure 3). Atoms O(3) and O(2) at $x - 1, y, z$ are in the apical positions. By means of bonds to four different NTA groups and a water molecule the sodium atoms help bind the structure together. The coordination of sodium rather than copper by water is not unusual. In the two other crystal structures analyzed where Cu(II), Na, and H_2O are all present, sodium glycylglycylglycinocuprate(II) monohydrate[14] and disodium glycylglycylglycylglycinocuprate(II) decahydrate,[15] only the sodium atoms are coordinated by water. In both examples the water bonds to sodium even though the octahedron about the copper atom is incomplete. A similar situation is found in LiCuNTA·$3H_2O$ where again all the solvation occurs at the alkali metal. Presumably in each case chelation of the Cu^{2+} ion neutralizes the ionic charge so that subsequent stabilization of the structure is best achieved by coordination of H_2O to the alkali metal. The water molecule is involved in only one hydrogen bond: O(W)-H(W1)· · ·O(5) at $-x, y - \frac{1}{2}, -z + \frac{1}{2}$, the O· · ·O distance being 2.80 Å and the angle at hydrogen, 161°.

NTA in Solution. The infrared spectra of solid NaCuNTA·H_2O can be compared with the absorption spectra of the Cu-NTA complex in D_2O solution.[16] For the solid, the strongest absorption occurs at 1590 cm^{-1}, a region characteristic of coordinated carboxylate groups.[17] In solution, the only peak in this region occurs at 1615 cm^{-1}. The lack of neighboring peaks or shoulders in the solution spectrum suggests that each of the carboxylate groups is equally coordinated to the copper atom. The chelated structure found in crystalline NaCuNTA·H_2O, therefore, is very likely the predominant form in solution. In aqueous solution, however, the two bonds from neighboring NTA groups are probably replaced by solvation molecules.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2286.

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