

Table 3. *Hydrogen-bond distances (Å) and angles (°)*

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$\angle D-H\cdots A$
$W(1)-H(11)\cdots W(4)$	0.971 (13)	1.832 (13)	2.801 (10)	174 (1)
$W(1)-H(12)\cdots O(12)$	0.921 (21)	2.094 (18)	2.969 (10)	158 (2)
$W(2)-H(21)\cdots O(13)$	0.935 (19)	1.837 (17)	2.767 (11)	172 (1)
$W(2)-H(22)\cdots O(11)$	0.959 (15)	2.068 (15)	2.944 (8)	151 (1)
$W(3)-H(31)\cdots O(22)$	0.895 (19)	2.521 (20)	3.100 (8)	123 (1)
$W(3)-H(32)\cdots W(4)$	1.005 (12)	1.847 (12)	2.848 (9)	174 (1)
$W(4)-H(41)\cdots O(23)$	0.960 (18)	1.933 (20)	2.870 (12)	165 (2)
$W(4)-H(42)\cdots O(21)$	0.952 (15)	2.233 (15)	3.100 (9)	151 (2)
		2.386 (22)	2.985 (12)	121 (2)

0.9 (2) Å. The other very weak hydrogen bond, H(31), whose coordinates were in some doubt in CMN, has a long ($H\cdots A$) distance 2.521 Å and is probably all ionic in character (*cf.* Baur, 1972). The coordinates of H(31) and H(32) are those whose values differ most in LMN compared to CMN, there being a slight twist about the $Mg(2)-W(3)$ axis.

Improving the resolution of the hydrogen-proton positions by refinement of the neutron diffraction data has shown LMN to be isostructural with CMN, with the exception of the H atoms of $W(3)$. That this is a real effect between the two compounds is doubtful; the discrepancy probably arises from the inherently poor resolution of H atom positions by X-ray methods.

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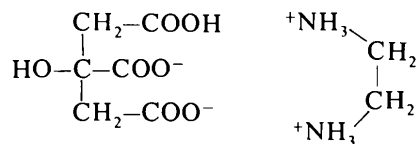
Ethylenediamine Citrate

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Abstract. $(\text{C}_6\text{H}_6\text{O}_7)^{2-}\cdot(\text{C}_2\text{H}_{10}\text{N}_2)^{2+}$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.642$ (2), $b = 9.933$ (1), $c = 6.794$ (1) Å, $\alpha = 110.69$ (1), $\beta = 106.53$ (1), $\gamma = 98.16$ (1)°, $V = 561.9$ (2) Å³, $D_m = 1.49$ (floatation in 1,1-dichloroethane and tetrachloroethylene), $D_x = 1.49$ g cm⁻³. The structural formula is



The structure was solved by direct methods (*MULTAN*) and refined by full-matrix least-squares procedures to a

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Table 1. *Refined atomic parameters for ethylenediamine citrate*

Positional parameters are listed as fractions of cell edges. Estimated standard deviations, obtained from the least-squares refinement, are given in parentheses for the last digits listed for any parameter.

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0.5761 (2)	0.2657 (1)	-0.2275 (2)
O(2)	0.6143 (2)	0.0396 (1)	-0.3307 (2)
O(3)	0.9858 (2)	0.1276 (1)	0.5407 (3)
O(4)	0.7634 (1)	0.0083 (1)	0.2745 (2)
O(5)	0.8058 (1)	0.5300 (1)	0.3079 (2)
O(6)	0.5742 (1)	0.4496 (1)	0.2923 (2)
O(7)	0.5776 (1)	0.1720 (1)	0.1673 (2)
C(1)	0.6456 (2)	0.1771 (2)	-0.1932 (3)
C(2)	0.7750 (2)	0.2242 (2)	0.0255 (3)
C(3)	0.7195 (2)	0.2714 (2)	0.2246 (3)
C(4)	0.8346 (2)	0.2762 (2)	0.4381 (3)
C(5)	0.8598 (2)	0.1244 (2)	0.4114 (3)
C(6)	0.6975 (2)	0.4295 (2)	0.2765 (3)
C(7)	0.2163 (2)	0.2316 (2)	0.2076 (3)
C(8)	0.2130 (2)	0.3350 (2)	0.0889 (3)
N(1)	0.3662 (2)	0.2615 (1)	0.3771 (3)
N(2)	0.2943 (2)	0.3042 (1)	-0.0700 (2)
H(1)	0.816 (2)	0.142 (2)	0.014 (3)
H(2)	0.845 (2)	0.307 (2)	0.037 (4)
H(3)	0.932 (2)	0.346 (2)	0.477 (3)
H(4)	0.793 (2)	0.307 (2)	0.553 (4)
H(5)*	0.554 (5)	0.018 (5)	-0.428 (7)
H(6)*	0.988 (6)	0.045 (5)	0.556 (9)
H(7)	0.601 (2)	0.096 (2)	0.183 (4)
H(8)	0.446 (3)	0.263 (3)	0.330 (5)
H(9)	0.387 (2)	0.360 (2)	0.504 (4)
H(10)	0.364 (2)	0.185 (2)	0.418 (4)
H(11)	0.266 (2)	0.354 (2)	-0.163 (4)
H(12)	0.265 (2)	0.194 (2)	-0.161 (4)
H(13)	0.397 (3)	0.338 (2)	-0.008 (4)
H(14)	0.188 (2)	0.135 (2)	0.101 (4)
H(15)	0.149 (2)	0.247 (2)	0.291 (4)
H(16)	0.261 (2)	0.432 (2)	0.191 (4)
H(17)	0.104 (2)	0.316 (2)	-0.006 (4)

* 50% occupancy.

final $R = 0.042$ (Mo $K\alpha$ data). There is extensive hydrogen bonding and disorder of H atoms in the hydrogen bonding between pairs of carboxyl groups. No more than two O atoms of any one citrate ion chelate to a given ethylenediamine cation.

Introduction. Triclinic crystals were prepared by dissolving 8 g citric acid monohydrate in water (~30 ml) and then slowly adding an equimolar amount of ethylenediamine dissolved in water (~5 ml). The solution was refluxed for 1 h and, upon cooling, was kept at 5 °C for about a week, when crystals appeared.

Three-dimensional data were collected on a Syntex automated diffractometer with monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) using the ω -scan technique. A crystal, ground as a sphere of diameter 0.17 mm, was used. Intensities were measured for 2580 unique reflections in the range $\sin \theta/\lambda = 0$ to 0.65 \AA^{-1} ($2\theta = 55^\circ$). Values for $\sigma(I)$ were derived from counting statistics and measured instrumental uncertainties. There were 691 reflections for which the measured intensity, I_o , was less than $2.3\sigma(I)$ and these were considered to be below the threshold of measurement. Values of $\sigma(F)$ for observed data were calculated from the formula $\sigma(F) = (F/2)\{[\sigma^2(I)/I^2] + \delta^2\}^{1/2}$, where δ is a measured instrumental uncertainty, 0.0320, determined from the variation in the intensities of the standard reflections. The intensity fall-off during data collection, as indicated by the periodically measured standard reflections, was negligible. The data were converted to structure amplitudes by application of Lorentz and polarization factors and placed on an absolute scale with a Wilson plot. No absorption correction was applied. The intensity statistics indicated a centrosymmetric structure.

The structure was solved by direct methods with the multiple-solution program *MULTAN* (Germain, Main

Table 2. *Some interatomic parameters*

(a) Interbond angles (°)

O(1)–C(1)–O(2)	124.6 (2)	O(4)–C(5)–C(4)	121.4 (1)	C(1)–C(2)–C(3)	109.9 (1)
O(1)–C(1)–C(2)	120.6 (1)	O(5)–C(6)–O(6)	124.6 (1)	C(3)–C(4)–C(5)	112.8 (1)
O(2)–C(1)–C(2)	114.8 (1)	O(5)–C(6)–C(3)	117.3 (1)	C(2)–C(3)–C(4)	111.1 (1)
O(3)–C(5)–O(4)	123.4 (1)	O(6)–C(6)–C(3)	118.1 (1)	C(4)–C(3)–C(6)	107.9 (1)
O(3)–C(5)–C(4)	115.2 (1)	O(7)–C(3)–C(6)	107.7 (1)	C(2)–C(3)–C(6)	109.3 (1)
		O(7)–C(3)–C(2)	110.3 (1)	C(8)–C(7)–N(1)	112.9 (1)
		O(7)–C(3)–C(4)	110.4 (1)	C(7)–C(8)–N(2)	113.4 (1)

(b) Torsion angles (°)

O(2)–C(1)–C(2)–C(3)	-116.8 (2)	C(5)–C(4)–C(3)–O(7)	59.6 (2)
O(1)–C(1)–C(2)–C(3)	61.2 (2)	C(5)–C(4)–C(3)–C(2)	-63.1 (2)
O(4)–C(5)–C(4)–C(3)	-24.9 (2)	C(5)–C(4)–C(3)–C(6)	177.1 (1)
O(3)–C(5)–C(4)–C(3)	155.5 (2)	C(4)–C(3)–C(6)–O(6)	-109.6 (2)
O(6)–C(6)–C(3)–O(7)	9.6 (2)	C(2)–C(3)–C(6)–O(5)	-53.0 (2)
O(5)–C(6)–C(3)–O(7)	-172.9 (1)	C(2)–C(3)–C(6)–O(6)	129.5 (2)
C(1)–C(2)–C(3)–C(4)	163.6 (1)	C(1)–C(2)–C(3)–O(7)	40.8 (2)
C(1)–C(2)–C(3)–C(6)	-77.4 (2)	N(1)–C(7)–C(8)–N(2)	71.4 (2)

& Woolfson, 1971) using 181 reflections with $E > 1.70$. The first E map gave the positions of all the heavy atoms. Subsequent isotropic then anisotropic full-matrix least-squares refinement reduced R to 0.08. At this point a difference Fourier synthesis was carried out and the positions of all the H atoms, including two disordered H atoms each with 50% occupancy, were located. Refinement of all atoms then proceeded, with H atoms treated isotropically and other atoms treated anisotropically. The final R value was 0.042 and the final weighted R value was 0.046.*

Scattering factors used for C, O and N were those listed in *International Tables for X-ray Crystallography* (1962) and those for H were from Stewart,

* Lists of structure factors, anisotropic temperature factors, equations of planes and angles between planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32914 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

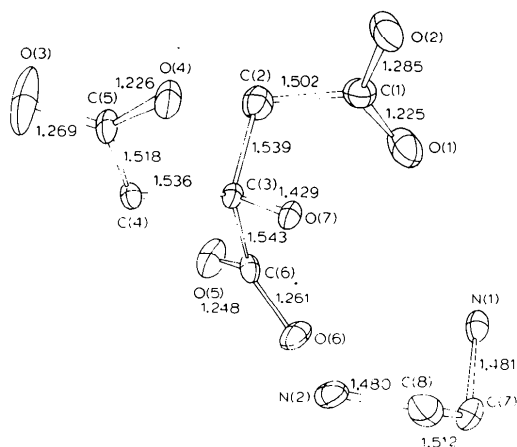


Fig. 1. Thermal motion in the citrate and ethylenediamine ions. Bond lengths (Å) in the hydrogen citrate ion are indicated. The estimated standard deviations of such bonds are about 0.002 Å.

Davidson & Simpson (1965). The positional parameters are given in Table 1. Computer programs used were *UCLALS4* (Gantzel, Sparks, Long & Trueblood, 1969), modified by Carrell (1975), the *CRYSNET* package (Bernstein *et al.*, 1974), and other programs written in the ICR Laboratory.

Discussion. The crystal structures of citric acid and several metal citrates have been determined in this and other laboratories (Nordman, Weldon & Patterson, 1960*a,b*; Glusker *et al.*, 1965; Johnson, 1965; Glusker, Minkin & Patterson, 1969; Gabe, Glusker, Minkin & Patterson, 1967; Roelofsen & Kanters, 1972; Glusker & Carrell, 1973; Carrell & Glusker, 1973*a,b*; Sheldrick, 1974; Mastropaolo, Powers, Potenza & Schugar, 1976; Strouse, Layten & Strouse, 1977). The structure determination of an ethylenediamine salt was undertaken in order to determine the chelation of such a cation by citrate.

Bond lengths are shown in Fig. 1, which also illustrates the thermal motion. Interbond angles and torsional angles are listed in Table 2. The central carboxyl group is ionized, but the two terminal carboxyl groups are disordered with respect to their state of ionization. The C—O bond lengths in these two carboxyl groups are unequal and are intermediate between the bond lengths in the average carboxylic acid and the carboxylate groups found in citrates (Glusker, 1968). The H atoms involved in the disorder, H(5) and H(6), each with an occupancy of one-half, were located on a difference map. Some disorder in O(3), as evidenced by a high value of B_{33} , has also been noted.

Strong hydrogen bonds are formed between O(2) and O(2ⁱⁱ) and between O(3) and O(3ⁱⁱ) with H(5) and H(6) disordered between them (Table 3, Fig. 2) (Carrell, 1976). Each ethylenediamine ion forms six strong hydrogen bonds. The cation spans the hydroxyl oxygen, O(7), and the central carboxylate oxygen, O(6), of one citrate ion. It also spans O(2^{iv}) and O(4^{iv}) of another

Table 3. *Hydrogen bonds*

D	H	A	D...A (Å)	H—D (Å)	H...A (Å)	∠A...H—D (°)	∠H—D...A (°)	∠H—D—C (°)
O(2)	H(5)*	O(2 ⁱ)	2.473 (2)	0.69 (4)	1.79 (4)	175 (4)	3 (3)	114 (3)
O(3)	H(6)*	O(3 ⁱⁱ)	2.470 (1)	0.86 (3)	1.69 (3)	149 (5)	21 (3)	114 (3)
O(7)	H(7)	O(4)	2.703 (1)	0.85 (1)	1.95 (1)	147 (1)	23 (1)	103 (1)
N(1)	H(8)	O(7)	2.872 (1)	0.91 (2)	2.02 (2)	156 (2)	17 (1)	117 (2)
N(1)	H(9)	O(6 ⁱⁱⁱ)	2.803 (2)	0.99 (2)	1.82 (2)	172 (2)	5 (1)	108 (1)
N(1)	H(10)	O(2 ^{iv})	2.934 (1)	0.89 (2)	2.16 (1)	145 (2)	25 (1)	107 (1)
N(2)	H(11)	O(5 ^v)	2.775 (1)	0.94 (2)	1.85 (1)	169 (2)	7 (1)	108 (1)
N(2)	H(12)	O(4 ^{iv})	2.810 (1)	1.00 (2)	1.83 (2)	168 (2)	8 (1)	108 (1)
N(2)	H(13)	O(6)	2.834 (2)	0.92 (2)	2.05 (2)	143 (2)	26 (2)	117 (2)

Symmetry-code superscripts: (i) $1 - x, -y, -1 - z$; (ii) $2 - x, -y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1 - x, -y, -z$; (v) $1 - x, 1 - y, -z$.

* The hydrogen bonding involving O(2) and O(3) may be described as a mixture: 50% occupancy: O(3ⁱⁱ)—H(6ⁱⁱ)...O(3) and O(2)—H(5)...O(2ⁱ); 50% occupancy: O(3ⁱⁱ)...H(6)—O(3) and O(2)...H(5)—O(2ⁱ). This corresponds to one H atom per asymmetric unit.

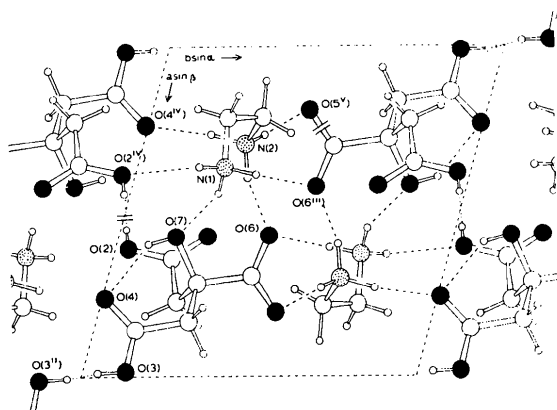


Fig. 2. Packing in the unit cell; view down *c*. The hydrogen-bond network is illustrated. The superscript nomenclature is given in Table 4. Oxygen atoms are black, and nitrogen atoms are stippled. Two solid lines crossing a bond indicate a translation of *c* for one of the two atoms involved in the bond. This diagram was drawn by the program *VIEW* (Carrell, 1976).

citrate ion. O(1) is not involved in any hydrogen bonding.

The angle between the plane of the central carboxyl group C(3)C(6)O(5)O(6) and the adjacent hydroxyl group C(6)C(3)O(7) is 8.42° [an angle which is always low in α -hydroxycarboxylic acids (Jeffrey & Parry, 1952; Newton & Jeffrey, 1977)]. Both of these planes are nearly perpendicular to the plane through the center backbone atoms C(2)C(3)C(4).

The conformation of the citrate ion is similar to that of calcium hydrogen citrate (Sheldrick, 1974), rubidium dihydrogen citrate (Nordman *et al.*, 1960*a*) and sodium dihydrogen citrate (Glusker *et al.*, 1965), rather than that of lithium ammonium hydrogen citrate (Gabe *et al.*, 1967), or magnesium or manganese citrates (Johnson, 1965; Carrell & Glusker, 1973*a*). In the latter group the citrate ion is fully extended, while in the first three citrates one terminal carboxyl group is rotated from the extended form. Analysis of some conformational parameters of the various citrates that have been studied crystallographically shows that the most constant angle is that between the hydroxyl plane O(7)C(3)C(6) and the plane of C(2)C(3)C(4) of the backbone of the molecule or ion. The plane of the central carboxyl group may rotate up to about 15° with respect to the plane of O(7)C(3)C(6), while the planes of the terminal carboxyl groups have much more freedom of rotation in order to form strong hydrogen bonds.

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