Contribution from the Department of Chemistry, University of Queensland, Brisbane, Australia

The Crystal Structure of (Hydrogen ethylenediaminetetraacetato)aquoferrate(III) and Gallate(III)

C. H. L. Kennard*

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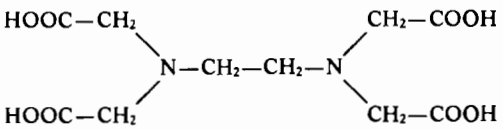
The crystal structure of (hydrogen ethylenediaminetetraacetato)-aquoferrate(III) has been determined using three dimensional x-ray diffraction data. There are four molecules in the monoclinic unit cell, space-group $P2_1/c$ with dimensions, $a = 8.36$, $b = 8.94$, $c = 17.83$ Å, $\beta = 99.5°$. In the structure, the ethylenediaminetetraacetic acid group wraps itself around the iron atom as a pentadentate ligand, leaving one uncomplexed carboxylic acid. A water molecule completes the octahedral co-ordination sphere surrounding the metal, (Fe-N, 2.22; Fe-O, 1.98; Fe-H_2O, 2.07 Å). The crystal structure of isomorphous (hydrogen ethylenediaminetetraacetato)-aquogallate(III) has also been refined ($a = 8.35$, $b = 8.84$, $c = 17.56$ Å, $\beta = 99.9°$, $P2_1/c$ $Z = 4$, Ga-N, 2.14; Ga-O, 1.95; Ga-H_2O, 1.95 Å).

Extensive knowledge has been recently accumulated about the stereochemistry of metal ions chelated by ethylenediaminetetraacetic acid (EDTA) (1).



(1)

Three dimensional structure determinations have shown that EDTA may co-ordinate to metal ions in a variety of ways. Firstly, it may complex as a pentadentate with one carboxlic acid free and protonated. This was found in the case of hydrogen (hydrogen ethylenediaminetetraacetato)-aquoniccolate(II),[1] H(NiH . EDTA . H_2O). As a sexadentate, EDTA completely surrounds a metal ion, e.g. in ammonium and rubidium ethylenediaminetetraacetatocobaltate(III)-dihydrate,[2] NH_4(CoEDTA)$2H_2O$; Rb(CoEDTA)$2H_2O$. Seven co-ordination of the metal ion in a NbF_7^{2-} [3] type configuration is found in tetraaquomanganese(II) di [(hydrogen ethylenediaminetetraacetato) aquomanganate(II)] - tetrahydrate[4] $[Mn(H_2O)_4]$-$[MnH.EDTA.H_2O]_2.4H_2O$. A similar structure occurs with the calcium salt of *trans*-1,2-diaminecyclohexane-N,N'-tetraacetatoaquoferrate(II),[5] $Ca(FeDCTA.H_2O)_2$-$8H_2O$, where the ethylene link between the amines is replaced by cyclohexane. Rubidium ethylenediaminetetraacetatoaquoferrate(III)-monohydrate,[6] Rb(FeEDTA . H_2O) . H_2O and lithium ethylenediaminetetraacetatoaquoferrate(III)-dihydrate,[7] Li(FeEDTA . H_2O) . $2H_2O$ are compounds where the metal ions are surrounded by EDTA and a water molecule in a pentagonal bipyramid configuration. With large metallic ions, such as lanthanum, nine and ten co-ordination is possible with water molecules completing the co-ordination, i.e. K(LaEDTA . $3H_2O$) . $5H_2O$ [8] and H(LaEDTA . $4H_2O$) . $3H_2O$.[9]

Busch and Bailar[10] have prepared dichloro(tetrahydrogen ethylenediaminetetraacetato)platinate(II)-pentahydrate, and suggest, from dissociation constants and infrared evidence, that EDTA behaves as a bidentate. They also propose from other results that EDTA in potassium (dihydrogen ethylenediaminetetraacetato) palladate(II)-monohydrate is tetradentate. This has recently been confirmed.[11] The structures of these two compounds are currently being investigated at the University of Queensland.

The structure of an ionic salt rubidium dihydrogen-ethylenediaminetetraacetate-dihydrate,[12] $Rb_2(H_2EDTA).2H_2O$, has also been determined.

The compounds dealt with in this paper, namely (hydrogen ethylenediaminetetraacetato)-aquoferrate-(III) and gallate(III), further extend the structural knowledge of EDTA as a multidentate chelating agent. A preliminary note has already been published,[13] and this also discussed the isomorphous (hydrogen ethylenediaminetetraacetato)-aquochromate(III).

(*) Department of Chemistry, University of Queensland, Brisbane, Australia.

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Experimental Section

Yellow crystals of (hydrogen ethylenediaminetetraacetato)-aquoferrate(III)-monohydrate, FeH . EDTA . H_2O, octahedral in shape, crystallised out of a solution formed when equi-molar quantities of a slurry of freshly precipitated iron(III) hydroxide and an aqueous suspension of EDTA were refluxed. (Found: C, 32.78; H, 4.12; Fe, 15.28; N, 7.69%. Calc. for $C_{10}H_{15}FeN_2O_9$: C, 33.08; H, 4.16; Fe, 15.38; N, 7.72%).

When an aqueous solution of these crystals was titrated with two moles of sodium hydroxide solution and the titration followed, at 25°C, using a pH meter, neutralisation occurred in two steps corresponding to the proposed mechanism:

$$(FeH \cdot EDTA \cdot H_2O) \underset{(pH\ 4.7)}{\overset{OH^-}{\rightleftharpoons}} (FeEDTA \cdot H_2O)^- + H_2O$$

$$OH^- \Big\| (pH\ 9.7)$$

$$(FeEDTA \cdot OH)^{2-} + 2H_2O$$

Infrared studies on the solid in potassium bromide pressed plates, using a Perkin-Elmer Infracord gave peaks at 1200 and 1758 cm^{-1}. Morris and Busch[14] characterised two peaks at 1228 and 1745 cm^{-1} in sodium nitro(hydrogenethylenediaminetetraacetato) cobaltate(III)-monohydrate as being due to an uncomplexed carboxylic acid.

Further evaporation of the original reaction solution yielded amber crystals of unknown composition. (Found: C, 28.45; H, 4.42; Fe, 18.46; N, 6.71%). A similar result has been reported by Lambert[15] and co-workers. This compound required only one mole of base, when titrated with sodium hydroxide, suggesting that the pentagonal bipyramid anion $(FeEDTA \cdot H_2O)^-$ was present. This hypothesis was strengthened when no infrared peak assigned to an uncomplexed carboxylic acid could be found. Although the iron analysis is somewhat high, the formula could be written as $[Fe(H_2O)_6]^{3+}$ $[FeEDTA \cdot H_2O]_3 \cdot H_2O$. (Calc. for $C_{30}H_{56}Fe_4N_6O_{34}$, C, 28.41; H, 4.45; Fe, 17.61; N, 6.63%).

Because the yellow crystals of FeH . EDTA H_2O were found to be twinned, a pyramid shaped crystal, ($0.1 \times 0.1 \times 0.2$ mm) was cut from the original octahedron, with the unique monoclinic axis, b, diagonal to the equatorial square. Low intensities, recorded due to the smallness of the cut crystal, caused a lack of accuracy in the final analysis. In order to obtain more accurate results, larger crystals of an isomorphous gallium compound were selected. These were kindly given by Dr. R.E. Sievers. Once again, a single crystal ($0.2 \times 0.2 \times 0.3$ mm) had to be cut from a large twin. (Found: C, 31.60; H, 4.12; N, 7.44%. Calc. for $C_{10}H_{15}GaN_2O_9$: C, 31.86; H, 4.01; N, 7.44%).

Crystal Data. $C_{10}H_{15}FeN_2O_9$, $M = 363.1$, monoclinic $a = 8.364 \pm 0.005$, $b = 8.942 \pm 0.005$, $c = 17.83 \pm 0.01$Å, $\beta = 99.46 \pm 0.05°$, $U = 1315$, $D_m = 1.83$ (by flotation), $Z = 4$, $D_c = 1.83$, $F(000) = 748$, space-group $P2_1/c$ (C_{2h}^5, No. 14); nickel filtered $Cu_{K\alpha}$ X-radiation for cell dimensions using Buerger precession camera; zirconium filtered $Mo_{K\alpha}$ X-radiation for data collection, using a goniostat type diffractometer; intensity maxima counted for twenty seconds with stationary crystal; overall background subtracted; 756 reflections had an intensity greater than background in the diffracting sphere up to $2\Theta = 65°$; 5° take off angle.

$C_{10}H_{15}GaN_2O_9$, $M = 377.0$, monoclinic, $a = 8.347 \pm 0.001$, $b = 8.840 \pm 0.001$, $c = 17.565 \pm 0.002$Å, $\beta = 99.86 \pm 0.01°$, $U = 1277$, $Z = 4$, $D_c = 1.96$, $F(000) = 768$; space group $P2_1/c$ (C_{2h}^5, No. 14); zirconium filtered $Mo_{K\alpha}$ X-radiation for cell dimensions and data collection, using a goniostat-type diffractometer; intensity maxima counted for ten seconds with stationary crystal; overall background subtracted; 3500 reflections had an intensity greater than background in the diffracting sphere up to $2\Theta = 65°$; 5° take off angle.

Intensity Data. The cell parameters measured, were used in computing goniostat settings. Intensities were counted for a given time at peak height. Overall background on either side of the reflection was subtracted from the peak count. Because the FeH . EDTA . H_2O crystal was less than 10% of the optimum volume, the error in the background played a big part in the error of the peak. This meant that, although high counts would be low in error, low counts would be in error by as much as a hundred percent.

In the case of GaH . EDTA . H_2O, the larger crystal selected gave five times the number of reflections. Accurate cell parameters were determined by measuring high angle axial reflections, using zirconium filtered molybdenum radiation, with the zero 2Θ angle being determined by averaging $\pm 2\Theta$.

Calculations. Structure factors and Fourier maps were calculated from programmes written for a Burroughs 220 computer. All other calculations were made on an IBM 709 using the X-ray 63 system.[16] The scattering factors used were those for C, N, O, Fe and Ga.[17] No correction was applied to the Fe and Ga scattering factors for anomalous dispersion in the presence of $Mo_{K\alpha}$ radiation. No correction was made for either absorption or extinction.

Structure Determination. In FeH . EDTA . H_2O atomic parameters for the iron atom were selected from an analysis of interatomic vectors in a three-dimensional F^2 synthesis to give an initial discrepancy factor, R, equal to 0.36. The other parameters were found from successive Fourier synthesis using the heavy atom approach. The variable parameters were refined after four cycles of least squares[18] with the Hughes weighting scheme[19] being applied. R equalled 0.17 for a refinement using all seven hundred and fifty-six observed reflections. With only the more intense four hundred and sixty nine reflections being considered, R

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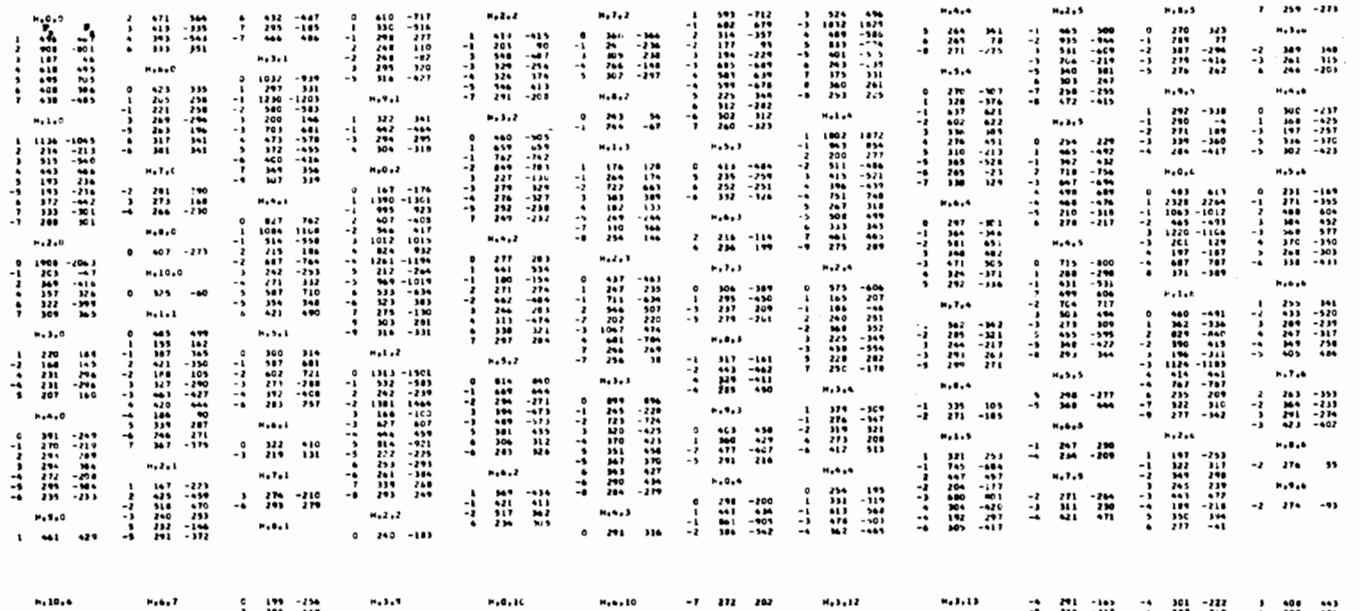
dropped to 0.12 with a slight increase in standard deviations. There was no appreciable difference in the two separate refinements. Atoms N(1) and C(5) had low temperature factors in both cases (N(1), 0.68, 0.85; C(5), 0.19, 0.26 Å^2 respectively). All results have been given in terms of the second refinement, although the complete reflection list is tabulated in Table I.

with the temperature factors being refined anisotropically, R reduced to 0.106%. Table II lists atomic coordinates for both complexes, which have been labelled as in Figure 1. Table III tabulates all the reflections observed. It should be noted that CrH. EDTA . H_2O[13] is also isomorphous, but, like the corresponding iron complex, forms extremely small twinned crystals.

Table I. Observed and calculated structure factors for (hydrogen ethylenediaminetetraacetato) aquoferrate(III).



Because the crystal selected was small, there was a high background in comparison to peak intensities. Consequently it was considered that the intense data would be more reliable. In this problem with twenty-two atoms per asymmetric unit larger than hydrogen, there were eighty nine parameters (x, y, z, B per atom; K overall scale factor). Naturally the more data collected, the greater the over-determination factor, and consequently the lower the error for each parameter. In order to overcome this poor refinement, larger crystals of an isomorphous compound, GaH.EDTA.H_2O were selected. Using coordinates from the refined FeH . EDTA . H_2O, GaH . EDTA . H_2O initially gave an R = 0.26. On full matrix least squares refinement

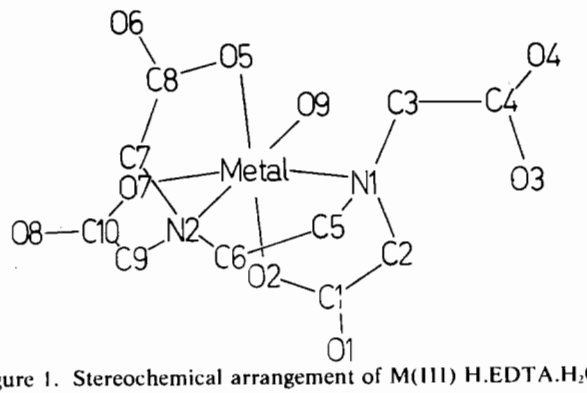


Figure 1. Stereochemical arrangement of M(III) H.EDTA.H_2O.

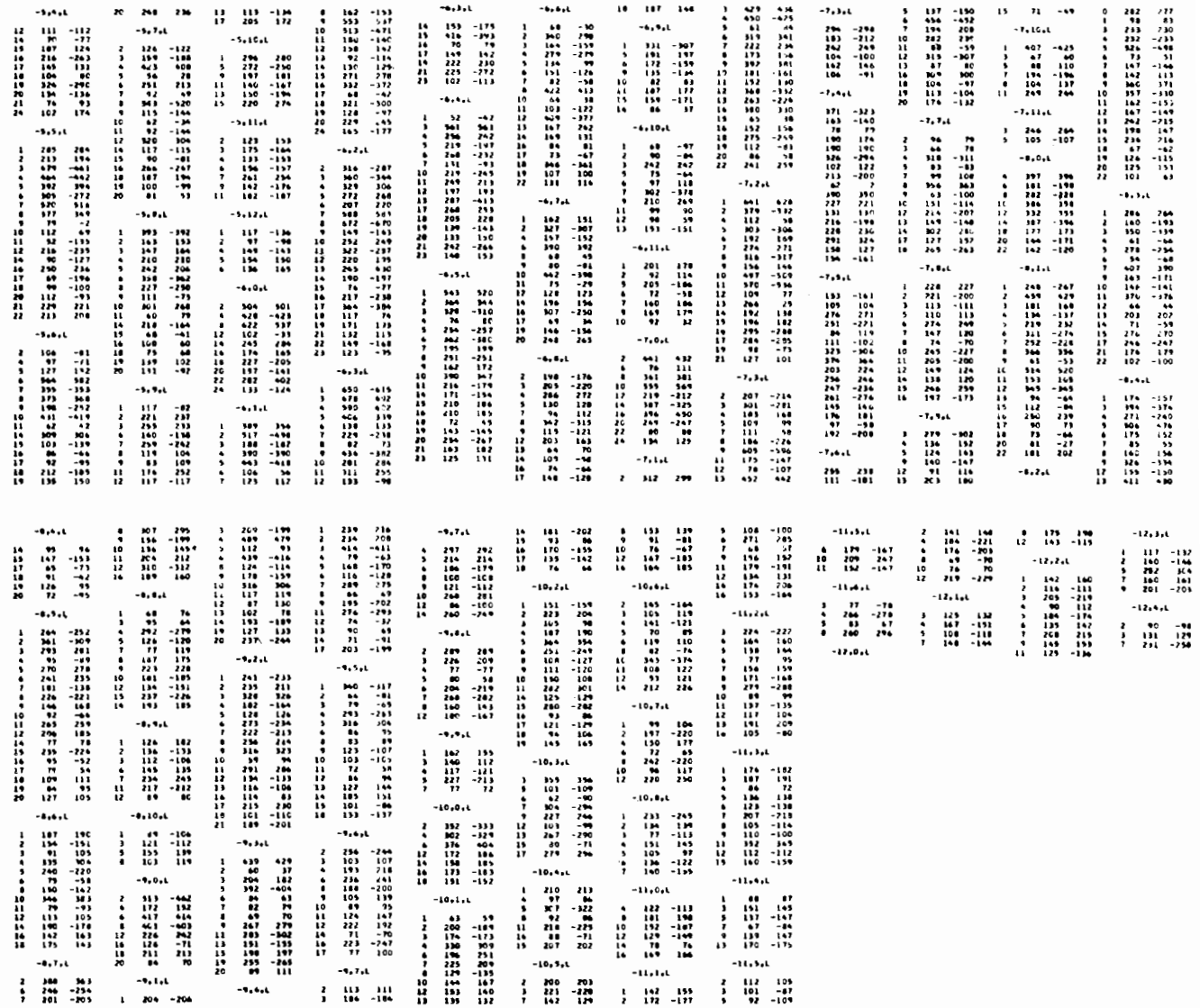
Table II. Positional parameters ($\times 10^4$). (Estimated standard deviations are given in brackets)

		FeH . EDTA . H_2O	GaH . EDTA . H_2O			FeH . EDTA . H_2O	GaH . EDTA . H_2O
M	x/a	1898.8 (8)	1928.1 (0.7)	O(9)	x/a	2185 (35)	2203 (6)
	y/b	1655.4 (8)	1750.7 (0.9)		y/b	−627 (34)	−420 (7)
	z/c	1429.0 (4)	1441.8 (0.3)		z/c	1319 (18)	1308 (2)
N(1)	x/a	3668 (34)	3659 (5)	C(1)	x/a	1144 (51)	1136 (8)
	y/b	2621 (36)	2661 (6)		y/b	2232 (46)	2163 (10)
	z/c	737 (19)	760 (2)		x/c	−191 (28)	−185 (3)
N(2)	x/a	1731 (41)	1711 (6)	C(2)	x/a	2877 (54)	2862 (9)
	y/b	3982 (36)	4015 (7)		y/b	2834 (52)	2736 (11)
	z/c	1790 (20)	1764 (2)		z/c	− 98 (28)	− 63 (4)
O(1)	x/a	374 (38)	398 (6)	C(3)	x/a	5030 (43)	5026 (8)
	y/b	2182 (32)	2104 (7)		y/b	1542 (50)	1582 (10)
	z/c	− 835 (20)	− 865 (2)		z/c	839 (20)	854 (4)
O(2)	x/a	548 (32)	529 (5)	C(4)	x/a	6474 (54)	6467 (8)
	y/b	1724 (38)	1838 (6)		y/b	2054 (54)	2129 (10)
	z/c	375 (16)	401 (2)		z/c	469 (28)	469 (4)
O(3)	x/a	7436 (37)	7443 (6)	C(5)	x/a	4038 (41)	4067 (9)
	y/b	915 (34)	912 (7)		y/b	4142 (41)	4195 (11)
	z/c	423 (18)	458 (2)		z/c	1133 (21)	1114 (4)
O(4)	x/a	6781 (38)	6731 (8)	C(6)	x/a	2570 (46)	2552 (10)
	y/b	3277 (45)	3338 (8)		y/b	4939 (44)	4962 (12)
	z/c	269 (18)	286 (3)		z/c	1274 (22)	1231 (4)
O(5)	x/a	3590 (36)	3628 (6)	C(7)	x/a	2589 (59)	2596 (10)
	y/b	1571 (42)	1599 (6)		y/b	4014 (51)	4091 (11)
	z/c	2307 (18)	2353 (3)		z/c	2554 (30)	2585 (4)
O(6)	x/a	4772 (42)	4819 (8)	C(8)	x/a	3686 (56)	3796 (9)
	y/b	2833 (38)	2873 (8)		y/b	2683 (55)	2739 (11)
	z/c	3330 (21)	3372 (3)		z/c	2774 (30)	2805 (4)
O(7)	x/a	− 118 (36)	2 (6)	C(9)	x/a	−1 (61)	− 22 (9)
	y/b	1649 (43)	1526 (6)		y/b	4224 (61)	4298 (10)
	z/c	1888 (16)	1896 (2)		z/c	1720 (30)	1728 (4)
O(8)	x/a	−2183 (43)	−2082 (7)	C(10)	x/a	−813 (46)	−773 (9)
	y/b	2920 (37)	2902 (7)		y/b	2919 (37)	2790 (10)
	z/c	2182 (21)	2241 (3)		z/c	1977 (22)	1977 (4)

Isotropic and anisotropic temperature factors (Å²), the latter in the form exp $[-1/4(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$. Estimated standard deviations are given in brackets)

	FeH . EDTA . H_2O	GaH . EDTA . H_2O					
	B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
M	1.8 (0.2)	1.07 (0.02)	1.20 (0.03)	1.54 (0.02)	− 0.08 (0.02)	0.16 (0.02)	0.00 (0.02)
N(1)	0.8 (0.6)	0.9 (0.1)	1.0 (0.2)	1.6 (0.1)	− 0.3 (0.1)	0.2 (0.1)	− 0.7 (0.2)
N(2)	1.9 (0.7)	1.3 (0.1)	1.1 (0.2)	2.4 (0.1)	0.0 (0.1)	0.3 (0.1)	− 0.1 (0.2)
O(1)	3.6 (0.8)	1.2 (0.1)	2.4 (0.2)	1.9 (0.1)	− 0.9 (0.1)	− 0.2 (0.1)	0.6 (0.2)
O(2)	3.0 (0.7)	1.0 (0.1)	2.1 (0.2)	2.0 (0.1)	− 0.2 (0.1)	0.3 (0.1)	0.2 (0.2)
O(3)	3.0 (0.7)	1.3 (0.1)	2.2 (0.2)	3.8 (0.1)	− 0.1 (0.1)	0.8 (0.1)	− 0.5 (0.2)
O(4)	4.0 (0.8)	2.4 (0.2)	3.2 (0.3)	3.7 (0.1)	0.1 (0.1)	1.1 (0.1)	1.0 (0.2)
O(5)	4.1 (0.7)	1.8 (0.1)	3.2 (0.3)	2.6 (0.1)	0.1 (0.1)	0.1 (0.1)	0.4 (0.2)
O(6)	4.7 (0.9)	3.5 (0.2)	2.5 (0.3)	3.0 (0.1)	0.9 (0.2)	− 1.0 (0.1)	− 1.1 (0.2)
O(7)	3.3 (0.7)	2.4 (0.1)	1.8 (0.2)	1.7 (0.1)	− 0.5 (0.1)	0.7 (0.1)	− 0.2 (0.2)
O(8)	5.2 (0.9)	2.1 (0.1)	2.9 (0.3)	3.6 (0.1)	− 0.2 (0.1)	0.7 (0.1)	− 0.2 (0.2)
O(9)	3.2 (0.7)	2.2 (0.1)	1.0 (0.2)	3.4 (0.1)	0.1 (0.1)	− 0.3 (0.1)	0.6 (0.2)
C(1)	2.1 (0.9)	0.7 (0.1)	1.1 (0.3)	0.6 (0.1)	0.1 (0.1)	− 0.2 (0.1)	0.2 (0.2)
C(2)	3.3 (1.2)	0.9 (0.2)	1.5 (0.3)	1.3 (0.1)	− 0.1 (0.2)	0.2 (0.1)	0.3 (0.2)
C(3)	1.6 (0.9)	1.2 (0.2)	0.8 (0.3)	1.2 (0.1)	0.0 (0.2)	0.4 (0.1)	0.0 (0.2)
C(4)	2.8 (1.1)	1.2 (0.1)	1.4 (0.2)	0.9 (0.1)	− 0.2 (0.1)	0.4 (0.1)	0.0 (0.2)
C(5)	0.3 (0.7)	1.4 (0.2)	1.0 (0.3)	0.9 (0.1)	0.0 (0.2)	0.3 (0.1)	0.2 (0.2)
C(6)	1.3 (0.8)	1.5 (0.2)	1.8 (0.4)	1.7 (0.1)	− 0.2 (0.2)	0.5 (0.1)	0.1 (0.2)
C(7)	3.3 (1.1)	1.7 (0.2)	2.0 (0.3)	1.4 (0.1)	0.2 (0.2)	0.3 (0.1)	0.1 (0.2)
C(8)	2.9 (1.0)	1.5 (0.2)	1.4 (0.3)	1.6 (0.1)	0.2 (0.2)	0.4 (0.1)	− 0.2 (0.2)
C(9)	3.7 (1.2)	1.3 (0.2)	1.0 (0.3)	1.0 (0.1)	0.0 (0.2)	0.2 (0.1)	− 0.3 (0.2)
C(10)	0.8 (0.8)	1.2 (0.2)	1.0 (0.3)	1.3 (0.1)	− 0.3 (0.2)	0.0 (0.1)	0.4 (0.2)

Table III. Observed and calculated structure factor for (hydrogen ethylenediaminetetraacetato)aquogallate(III)



Discussion

Table IV lists the interatomic distances and angles. Table V lists plane equations of five member chelate rings and compares these results with other EDTA structures.

Ethylenediaminetetraacetic acid behaves as a pentadentate in complexes of the type M(III).(H.EDTA).H_2O, where M(III) = Fe(III) and Ga(III). The coordination sphere may best be described in terms of a regular octahedron with a water molecule filling the sixth position. The octahedron is slightly distorted as plane [M, N(1), N(2), O(7), O(9)] intersects plane [M, N(1), O(2), O(7), O(5)] at 88° and 88.3° [FeH . EDTA . H_2O and GaH . EDTA . H_2O respectively], and intersects plane [M, N(2), O(2), O(9), O(5)] at 89° and 88.9°. These last two planes intersect at 90° and 88.4°.

Structure analysis has shown two Fe(III)-EDTA species. At low pH, the metal ion is surrounded in a regular octahedral arrangement by one water molecule and five of the six EDTA links. The sixth link, a carboxylic acid, is left protonated. With the addition of an equimolar amount of base, this proton is removed, and the carboxyl group is forced into the coordination sphere producing, around the Fe(III), a pentagonal bipyramid.

Perhaps the most important difference between the acid form (FeH . EDTA . H_2O) and its salt[6,7] $(Fe . EDTA . H_2O)^-$ is that in the former interatomic distances M-N and $M-O_G$ are slightly shorter [2.22 (0.03), 1.99 (0.03), as against 2.317 (0.012), 2.078 (0.012) for the Rubidium salt and 2.325 (0.003), 2.119 (0.003) Å for the Lithium one, respectively]. The $M-O_R$ and $M-O_{H_2O}$ links are similar [1.99 (0.03), 2.07 (0.03), as against 1.993 (0.011), 2.106 (0.011) for Rubidium and 1.969 (0.003), 2.107 (0.003) Å for the Lithium salt respectively]. The links $M-O_G$ and $M-O_R$ denote the equatorial and polar coordination of different carboxylic acids respectively in EDTA where the ethylenediamine-metal chelation is about the equator of the octahedral arrangement.

From an analysis of all the results, GaH . EDTA . H_2O is not only isomorphous but isostructural with FeH . EDTA . H_2O. All the metal-ligand distances are significantly shorter except $M-O_R$. In this case they are similar [1.98 (0.03), 1.974 (0.004)]. This suggests that

Table IV. Interatomic distances (Å)

	FeH . EDTA . H_2O	GaH . EDTA . H_2O
M-N(1)	2.25 (0.03)*	2.182 (0.005)
M-N(2)	2.19 (0.03)	2.097 (0.006)
M-O(2)	2.03 (0.03)	1.996 (0.004)
M-O(5)	1.93 (0.03)	1.953 (0.005)
M-O(7)	1.99 (0.03)	1.924 (0.005)
M-O(9)	2.07 (0.03)	1.951 (0.006)
C(1)-O(2)	1.28 (0.06)	1.255 (0.008)
C(8)-O(5)	1.29 (0.06)	1.276 (0.010)
C(10)-O(7)	1.30 (0.05)	1.311 (0.010)
C(1)-O(1)	1.22 (0.06)	1.248 (0.007)
C(8)-O(6)	1.24 (0.06)	1.201 (0.008)
C(10)-O(8)	1.26 (0.06)	1.263 (0.009)
C(4)-O(3)	1.31 (0.06)	1.351 (0.010)
C(4)-O(4)	1.19 (0.06)	1.148 (0.011)
N(1)-C(2)	1.54 (0.06)	1.486 (0.007)
N(1)-C(3)	1.48 (0.05)	1.476 (0.009)
N(2)-C(7)	1.43 (0.06)	1.506 (0.008)
N(2)-C(9)	1.45 (0.06)	1.459 (0.009)
N(1)-C(5)	1.54 (0.05)	1.506 (0.011)
N(2)-C(6)	1.51 (0.06)	1.514 (0.011)
C(5)-C(6)	1.48 (0.05)	1.480 (0.012)
C(1)-C(2)	1.53 (0.06)	1.507 (0.010)
C(3)-C(4)	1.54 (0.06)	1.555 (0.010)
C(7)-C(8)	1.52 (0.07)	1.565 (0.013)
C(9)-C(10)	1.46 (0.07)	1.566 (0.012)
Interatomic Angles (in degrees)		
N(1)-M-N(2)	83 (1)	83.8 (0.2)
N(1)-M-O(7)	155 (1)	160.9 (0.1)
N(1)-M-O(9)	103 (2)	101.2 (0.2)
N(1)-M-O(2)	78 (1)	79.7 (0.1)
N(1)-M-O(5)	90 (1)	91.0 (0.2)
N(2)-M-O(7)	77 (1)	82.5 (0.2)
N(2)-M-O(9)	168 (1)	171.4 (0.3)
N(2)-M-O(5)	83 (1)	85.9 (0.2)
N(2)-M-O(2)	101 (1)	98.4 (0.2)
O(7)-M-O(9)	99 (1)	94.2 (0.2)
O(7)-M-O(5)	103 (2)	101.2 (0.2)
O(7)-M-O(2)	90 (1)	89.2 (0.1)
O(9)-M-O(5)	88 (1)	87.0 (0.2)
O(9)-M-O(2)	90 (1)	89.4 (0.2)
O(5)-M-O(2)	167 (1)	169.2 (0.2)
O(4)-C(4)-O(3)	122 (5)	126.3 (1.0)
O(3)-C(4)-C(3)	105 (4)	105.8 (0.7)
O(4)-C(4)-C(3)	133 (6)	127.6 (1.1)
O(1)-C(1)-O(2)	127 (5)	124.9 (0.7)
O(1)-C(1)-C(2)	114 (4)	117.0 (0.8)
O(2)-C(1)-C(2)	122 (5)	118.1 (0.7)
C(4)-C(3)-N(1)	110 (4)	113.1 (0.7)
C(1)-C(2)-N(1)	108 (4)	112.4 (0.6)
C(3)-N(1)-C(2)	108 (3)	110.3 (0.6)
C(3)-N(1)-C(5)	114 (3)	114.9 (0.8)
C(3)-N(1)-M	102 (2)	105.8 (0.4)
C(2)-N(1)-C(5)	114 (4)	113.1 (0.7)
C(2)-N(1)-M	111 (2)	108.8 (0.3)
C(5)-N(1)-M	111 (2)	108.8 (0.3)
O(5)-C(8)-O(6)	120 (5)	125.5 (1.0)
C(7)-C(8)-O(6)	125 (6)	117.6 (1.0)
C(7)-C(8)-O(5)	118 (5)	116.9 (0.8)
O(7)-C(10)-O(8)	124 (5)	125.5 (1.0)
C(9)-C(10)-O(8)	124 (6)	116.6 (0.9)
C(9)-C(10)-O(7)	115 (5)	117.9 (0.8)
C(8)-C(7)-N(2)	115 (5)	113.0 (0.8)
C(10)-C(9)-N(2)	111 (4)	106.4 (0.7)
C(9)-N(2)-C(7)	113 (5)	110.7 (0.6)
C(9)-N(2)-C(6)	116 (5)	116.2 (0.8)
C(9)-N(2)-M	103 (3)	106.4 (0.4)
C(7)-N(2)-C(6)	115 (5)	111.3 (0.7)
C(7)-N(2)-M	105 (3)	104.4 (0.4)
C(6)-N(2)-M	107 (3)	106.9 (0.5)
M-O(2)-C(1)	121 (4)	120.3 (0.5)
M-O(7)-C(10)	118 (3)	114.8 (0.5)
M-O(5)-C(8)	117 (4)	116.3 (0.6)

* Standard deviation in Å.

Table V. Least squares plane equations of five member chelate rings, and the deviations of atoms from the ring

Ring	FeH . EDTA . H_2O Constant	Value (Å)	Atom	Deviation (Å)	GaH . EDTA . H_2O Constant	Value (Å)	Atom	Deviation (Å)
E	A	0.56	Fe	−0.03	A	0.54	Ga	−0.02
	B	−0.14	N(1)	0.17	B	−0.11	N(1)	0.17
	C	0.82	C(5)	−0.31	C	0.84	C(5)	−0.32
	D	2.46	C(6)	028	D	2.53	C(6)	0.28
			N(2)	−0.11			N(2)	−0.12
R1	A	−0.34	Fe	0.03	A	−0.32	Ga	0.03
	B	0.93	O(2)	−0.01	B	0.94	O(2)	−0.05
	C	0.18	C(1)	−0.02	C	0.15	C(1)	0.05
	D	1.44	C(2)	0.05	D	1.46	C(2)	−0.01
			N(1)	−0.05			N(1)	−0.02
R2	A	−0.79	Fe	−0.11	A	−0.81	Ga	−0.08
	B	−0.37	N(2)	0.16	B	−0.35	N(2)	0.12
	C	0.48	C(7)	−0.15	C	0.47	C(7)	−0.12
	D	−0.36	C(8)	0.01	D	−0.39	C(8)	0.03
			O(5)	0.09			O(5)	0.05
G2	A	0.27	Fe	0.16	A	0 28	Ga	0.16
	B	−0.07	N(2)	−0.26	B	−0.02	N(2)	−0.24
	C	0.96	C(9)	0.27	C	0.96	C(9)	0.22
	D	2.79	C(10)	−0.11	D	2.85	C(10)	−0.03
			O(7)	−0.06			O(7)	−0.11

The equation of the plane is expressed as $AI+BJ+CK=D$, where I, J and K are the fractional coordinates of the atoms in orthogonal angstrom space.

Comparison of interatomic distances (Å) in EDTA complexes

	1 (FeH.EDTA.H_2O) [a]	2 (GaH.EDTA.H_2O) [a]	3 (NiH.EDTA.H_2O)$^-$ [b]	4 (CoEDTA)$^-$ [b]	5 (MnH.EDTA.H_2O)$^{--}$ [b]	6 (FeDCTA.H_2O)$^-$ [b]	7 (FeEDTA.H_2O)$^-$ [a]	8 (FeEDTA.H_2O)$^-$	9 (LaEDTA.$3H_2O$)$^-$ [a]	10 (LaEDTA.$4H_2O$)$^-$ [a]
M-N	2.22 (0.03)	2.140 (0.006)	2.10	1.925, 1.93	2.377 (0.004)	2.290 (0.004)	2.317 (0.012)	2.325 (0.003)	2.865 (0.004)	2.755 (0.005)
M-O_R	1.98 (0.03)	1.974 (0.004)	2.04	1.885, 1.895	—	—	1.993 (0.011)	1.969 (0.003)	—	—
M-O_G	1.99 (0.03)	1.924 (0.005)	2.16	1.915, 1.915	—	—	2.078 (0.012)	2.119 (0.003)	—	—
M-O	—	—	—	—	2.236 (0.005)	2.054 (0.004)	—	—	2.555 (0.003)	2.507 (0.005)
M-O_w	2.07 (0.03)	1.951 (0.006)	2.08	—	2.155 (0.013)	2.090 (0.003)	2.106 (0.011)	2.107 (0.003)	2.592 (0.004)	2.580 (0.006)
C-C_{ester}	1.48 (0.05)	1.480 (0.012)	1.52	1.53, 1.54	1.518 (0.008)	1.526 (0.07)	1.503 (0.022)	1.502 (0.006)	[b]	[b]
C-C_{uester}	1.51 (0.06)	1.548 (0.012)	1.52	1.53, 1.54	1.519 (0.008)	1.523 (0.006)	1.497 (0.025)	1.519 (0.006)	[b]	[b]
C-N	1.49 (0.06)	1.491 (0.009)	1.49	1.49, 1.48	1.471 (0.007)	1.492 (0.006)	1.475 (0.022)	1.472 (0.005)	[b]	[b]
C-O_c	1.29 (0.06)	1.281 (0.009)	1.26	1.30, 1.29	1.250 (0.008)	1.273 (0.006)	1.299 (0.021)	1.272 (0.005)	1.261, 1.210 (0.004)	[b]
C-O_u	1.24 (0.06)	1.237 (0.008)	1.25	1.22, 1.19	1.263 (0.009)	1.233 (0.005)	1.222 (0.022)	1.230 (0.007)	1.249, 1.288 (0.006)	[b]
C=O	1.19 (0.06)	1.148 (0.011)	1.26	—	—	—	—	—	—	—
C-O_{un}	1.31 (0.06)	1.351 (0.010)	1.31	—	—	—	—	—	—	—
Ring	Atom	Deviations of atoms from least squares plane and angles between these planes								
E	M	−0.03	−0.02	−0.01	−0.02	0.01	−0.01	0.00		
	N	0.17	0.17	0.16	0.15	0.12	0.14	0.15		
	C	−0.31	−0.32	−0.31	−0.26	−0.26	−0.27	−0.29		
	C	0.28	0.28	0.32	0.24	0.27	0.26	0.28		
	N	−0.11	−0.12	−0.16	−0.11	−0.14	−0.13	−0.14		
R_1	M	0.03	0.03	0.07	0.07			0.10		
	N	−0.01	−0.05	−0.11	−0.05			−0.07		
	C	−0.02	0.05	0.10	0.01			0.01		
	C	0.05	−0.01	−0.02	0.07			0.13		
	O	−0.05	−0.02	−0.05	−0.10			−0.17		
R_2	M	−0.11	−0.08	−0.04	−0.07			−0.07		
	N	0.16	0.12	0.03	0.10			0.12		
	C	−0.15	−0.11	0.00	−0.09			−0.13		
	C	0.01	0.03	−0.05	0.01			0.05		
	O	0.09	0.05	0.06	0.05			0.05		
G_1	M				−0.21			−0.18		
	N				0.27			0.27		
	C				−0.22			0.25		
	C				0.00			−0.01		
	O				0.16			0.16		
G_2	M	0.16	0.16	0.18	0.23			0.19		
	N	−0.26	−0.24	−0.28	−0.28			0.28		
	C	0.27	0.22	0.24	0.21			0.29		
	C	−0.11	−0.03	0.01	0.03			0.02		
	O	−0.06	−0.11	−0.15	−0.18			−0.19		
E ∧ G_1		—	—	—	15.59°			14.25°		
E ∧ G_2		19.33°	17.23°	17.87°	17.25			14.43		
E ∧ R_1		79.71	81.18	86.48	84.25			82.54		
E ∧ R_2		89.78	89.99	82.42	89.58			89.31		
R_1 ∧ R_2		89.57	89.72	88.86	82.07			82.07		
G_1 ∧ G_2		—	—	—	1.85			1.41		

[a] Work reported in this paper. [b] Not reported, R ring type oxygen, G ring type oxygen, c complexed oxgen, u uncompleed oxygen.

because the covalent radii of Ga(III) is smaller than Fe(III), the closing of the R link in the former case is geometrically more difficult.

On closer examination, these structures have some interesting features. In the ethylenediamine link (E), carbon atoms are distributed evenly above and below the plane of the five membered ring by as much as 0.3 Å (Table V). The two ring complexed carboxylic acid-metal groups (R), which are above and below the (E) plane are at right angles to one another [89.6, 89.76°, FeH . EDTA . H_2O, GaH . EDTA . H_2O respectively] and at 79.7°, 89.0° [FeH . EDTA . H_2O] and 81.2°, 89.99° [GaH . EDTA . H_2O] to the E plane. However, the plane of the carboxylic acid-metal group (G) is not parallel to the E plane but distorted [19.3°, 17.23°]. Therefore R and G planes do not intersect at right angles but at 73.9°, and 76.20°.

An extensive hydrogen bonding system holds these molecules together. Table VI lists the various contacts. The water molecule represented by O(9), which completes the octahedral coordination around the metal atom, is linked to a carboxyl group O(1) through a centre of symmetry. The molecules are linked along the a axis by a hydrogen bond between the free carboxylic acid and a carboxylic group O(2). Figure 2 shows the packing. There is no close link about the two fold screw axis.

Table VI. Significant intermolecular contacts

	FeH . EDTAH_2O	GaH . EDTA . H_2O
O(2) ... $O(3)_I$	2.71	2.72
O(7) ... $O(3)_I$	3.11	3.06
O(1) ... $O(9)_{II}$	2.64	2.64
O(3) ... $O(9)_{III}$	3.16	3.19

The subscripts refer to the positions

I $-1+x,y,z$
II $-x,-y,-z$
III $1-x,-y,-z$

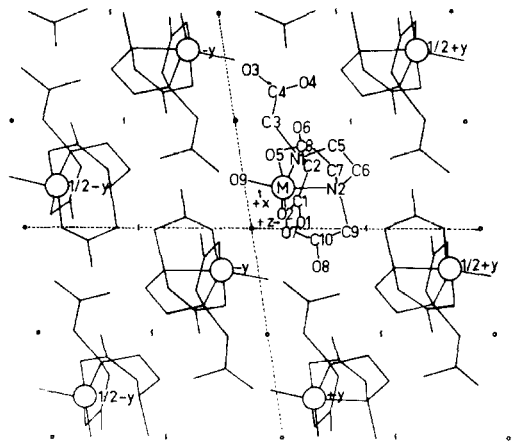


Figure 2. Packing of the M(III)H.EDTA . H_2O motif perpendicular to the unique axis.

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