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A Redetermination of Sodium Aqua[ethylenediaminetetraacetato(4−)]ferrate(III) Dihydrate, Na[Fe($C_{10}H_{12}N_2O_8$)(H_2O)].$2H_2O$

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Abstract. $M_r = 421\cdot1$, *Cc*, $a = 8\cdot895\,(1)$, $b = 11\cdot924\,(2)$, $c = 15\cdot043\,(2)$ Å, $\beta = 100\cdot06\,(1)^\circ$, $V = 1571\cdot0\,(4)$ Å^3, $Z = 4$, $D_m = 1\cdot73\,(3)$, $D_x = 1\cdot78$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot05$ mm^{-1}, $F(000) = 868$, $T = 293\,(2)$ K, $R = 0\cdot027$ for 2370 observed unique reflections. The anionic complex is 7-coordinate with a hexadentate ethylenediaminetetraacetate(4−) ligand. A water molecule on a pseudo twofold axis completes the coordination sphere. The unit-cell volume found here is 7% larger than that reported for this compound in an earlier and less-precise study. There are a number of significant differences between the two determinations in many of the bond lengths and bond angles found.

Introduction. During the workup of a reaction mixture containing sodium azide and aqua[ethylenediaminetetraacetato(3−)]iron(III), [Fe($C_{10}H_{13}N_2O_8$)(H_2O)], in ethanol–water, brown crystals were obtained which were analyzed as sodium aqua[ethylenediaminetetraacetato(4−)]ferrate(III) {Na[Fe(edta)(H_2O)]} {calc. for Na[Fe($C_{10}H_{12}N_2O_8$)(H_2O)].$2H_2O$: C 28·50, H 4·31, N 6·65; found: C 28·74, H 4·35, N 6·97%}. However, the unit-cell volume from our X-ray analysis [$V = 1571\cdot0\,(4)$ Å^3] and the density (1·73 Mg m^{-3}) differed markedly from those reported previously for this compound [Novozhilova, Polynova & Porai-Koshits (1975): $V = 1461\,(12)$ Å^3, $D_m = 1\cdot90$, $D_x = 1\cdot93$ Mg m^{-3}]. Authentic Na[Fe($C_{10}H_{12}N_2O_8$)(H_2O)].$2H_2O$ synthesized directly from $FeCl_3.6H_2O$ and edta also gave crystals with a measured density less than that reported (1·78 Mg m^{-3}). In order to ascertain whether the compound which had been obtained in our original reaction was indeed Na[Fe($C_{10}H_{12}N_2O_8$)(H_2O)].$2H_2O$, a complete X-ray structure determination was carried out. Since the parameters we find differ significantly from those reported in the earlier less-precise determination, we are reporting our results here.

Experimental. Densities measured by flotation (dibromomethane/carbon tetrachloride), approximately cubic crystal with 0·28 mm side, Syntex *P*3/*F* diffractometer with graphite monochromator, lattice parameters from 25 reflections ($10 < 2\theta < 35^\circ$), ω scan, scan range of 0·95° below and 1·1° above $\omega(0)$ for each reflection, background-counting-time/total-scan-time ratio 0·5, 3 standard reflections every 141 reflections (2% variation), 4983 reflections ($+h$, $\pm k$, $\pm l$, $1\cdot0 \leq 2\theta \leq 60\cdot0^\circ$), 2433 unique ($R_{\rm int} = 0\cdot15$ for merge), 63 unobserved [$|F| < 2\cdot5\sigma(F)$], empirical absorption correction based on ψ scans, min. and max. transmission coefficients 0·439 and 0·463, no secondary extinction correction, space group assigned from systematic absences *hkl*, $h+l = 2n+1$ and *h*0*l*, $l = 2n+1$ (model based on alternative assignment of space group as *C*2/*c* failed to converge satisfactorily). All computer programs from *SHELXTL* (Sheldrick, 1981), scattering-factor and anomalous-dispersion data from *International Tables for X-ray Crystallography* (1974). A sharpened Patterson map was interpreted for an iron atom in a general position in *Cc* or on a twofold axis in *C*2/*c*; structure was solved in *Cc* by phasing on Fe atom to produce a recognizable fragment of the molecule in a subsequent Fourier map; isotropic refinement on *F*, no hydrogen atoms included, gave $R = 0\cdot071$; all hydrogen atoms included with isotropic thermal parameters of 1·2 times $U_{\rm eq}$ of atoms to which they were attached, no hydrogen parameters refined here or in any subsequent steps, hydrogen atoms attached to carbon atoms idealized and fixed using a riding model with a fixed C—H distance, water hydrogen atoms found in a difference map. This model refined to $R = 0\cdot035$ with anisotropic thermal parameters for all nonhydrogen atoms. Since the space group *Cc* is polar in *x* and *z*, there was a problem of correct orientation with respect to these axes. If the wrong orientation were refined, a significant *x*-coordinate error would be expected since only $h \geq 0$ data are available (Cruickshank & McDonald, 1967). Refining a second model with the signs of the *x* and *z* coordinates reversed resulted in a significantly lower value of the generalized *R* factor (Hamilton, 1965): $R^G = 0\cdot038$ compared to $R^G = 0\cdot050$. The R^G factor ratio was 1·31 which well exceeded $\mathscr{R}_{1,2000,0.005}$

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(= 1·002) in Hamilton's $\mathscr{R}$ test. This indicated that this second model represented a significant improvement at the 99·5% confidence level. The averaged coordinate shifts due to this polar dispersion error (Zalkin, Hopkins & Templeton, 1966) were 0·028, 0·001 and 0·002 Å relative to Fe in x, y, and z. The resulting bond length and angle differences between the two models ranged from 0·00 to 0·03 Å and from 0·0 to 1·5°. The largest differences were obtained from bond lengths and angles involving the iron atom. There were no differences larger than twice the e.s.d. for bond lengths or bond angles involving only atoms other than iron for the two models. Anisotropic refinement on all non-H atoms with the correct model converged to $R = 0{\cdot}027$ and $wR = 0{\cdot}029$ [$w^{-1} = \sigma(F)^2 + |g|F_o^2$, $g = 0{\cdot}00209$]; $S = 0{\cdot}69$, 2370 observations, 224 variables; max. and min. peak heights in final difference maps 0·41 and −0·50 e Å^{-3}; max. and mean Δ/σ 0·007 and 0·002. The final fractional coordinates and U_{eq} values of the refined atoms are listed in Table 1.*

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ with the U_{ii}'s in an orthogonal coordinate system (Willis & Pryor, 1975).

	x	y	z	U_{eq}(Å^2)
Na(1)	0·38953 (13)	0·03126 (9)	0·35951 (7)	0·0242 (3)
Fe	0·00000	0·08911 (2)	0·50000	0·0152 (1)
N(1)	0·1700 (3)	0·1964 (2)	0·5996 (1)	0·0199 (5)
N(2)	−0·1442 (3)	0·1847 (2)	0·5899 (1)	0·0193 (5)
C(1)	0·0963 (3)	0·2727 (2)	0·6574 (2)	0·0268 (7)
C(2)	−0·0485 (3)	0·2198 (2)	0·6765 (2)	0·0228 (6)
C(3)	0·2621 (3)	0·1099 (2)	0·6545 (2)	0·0245 (7)
C(4)	0·1728 (3)	0·0034 (2)	0·6632 (2)	0·0196 (6)
C(5)	0·2626 (3)	0·2608 (2)	0·5457 (2)	0·0244 (7)
C(6)	0·2868 (3)	0·1924 (2)	0·4647 (2)	0·0216 (6)
C(7)	−0·2653 (3)	0·1074 (3)	0·6061 (2)	0·0241 (7)
C(8)	−0·3228 (3)	0·0429 (2)	0·5200 (2)	0·0202 (6)
C(9)	−0·2114 (3)	0·2820 (2)	0·5344 (2)	0·0264 (7)
C(10)	−0·1692 (3)	0·2884 (2)	0·4414 (2)	0·0190 (6)
O(1)	0·0553 (2)	−0·0153 (2)	0·6022 (1)	0·0213 (5)
O(2)	0·2200 (3)	−0·0622 (2)	0·7250 (1)	0·0282 (5)
O(3)	0·2024 (2)	0·1054 (2)	0·4477 (1)	0·0224 (5)
O(4)	0·3835 (3)	0·2233 (2)	0·4194 (2)	0·0320 (6)
O(5)	−0·2253 (2)	0·0309 (2)	0·4675 (1)	0·0236 (5)
O(6)	−0·4538 (2)	0·0035 (2)	0·5063 (2)	0·0289 (6)
O(7)	−0·0639 (2)	0·2220 (2)	0·4242 (1)	0·0239 (5)
O(8)	−0·2313 (2)	0·3586 (2)	0·3869 (1)	0·0249 (5)
O(9)	0·0018 (2)	−0·0474 (2)	0·4096 (1)	0·0237 (5)
O(10)	0·6006 (3)	−0·0206 (3)	0·2938 (2)	0·0444 (8)
O(11)	0·5426 (4)	−0·2525 (3)	0·2562 (2)	0·0463 (8)

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Fe—N(1)	2·318 (2)	C(8)—O(5)	1·279 (3)
Fe—N(2)	2·319 (2)	C(6)—O(3)	1·280 (3)
Fe—O(1)	1·972 (2)	C(4)—O(1)	1·284 (3)
Fe—O(7)	1·977 (2)	C(10)—O(7)	1·287 (3)
Fe—O(3)	2·096 (2)	C(8)—O(6)	1·240 (3)
Fe—O(5)	2·096 (2)	C(6)—O(4)	1·244 (4)
Fe—O(9)	2·122 (2)	C(4)—O(2)	1·232 (3)
N(1)—C(1)	1·487 (4)	C(10)—O(8)	1·232 (3)
N(2)—C(2)	1·487 (3)	C(7)—C(8)	1·516 (4)
N(1)—C(3)	1·477 (3)	C(5)—C(6)	1·512 (4)
N(2)—C(9)	1·491 (3)	C(9)—C(10)	1·514 (4)
N(1)—C(5)	1·470 (4)	C(3)—C(4)	1·515 (4)
N(2)—C(7)	1·470 (4)	C(1)—C(2)	1·506 (4)
O(5)—Fe—N(2)	72·3 (1)	Fe—N(2)—C(7)	106·5 (2)
O(3)—Fe—N(1)	71·7 (1)	Fe—N(1)—C(5)	107·3 (1)
O(7)—Fe—N(2)	79·0 (1)	Fe—N(2)—C(9)	105·4 (2)
O(1)—Fe—N(1)	78·4 (1)	Fe—N(1)—C(3)	102·2 (1)
O(5)—Fe—O(7)	88·0 (1)	Fe—N(2)—C(2)	111·0 (2)
O(5)—Fe—O(1)	94·1 (1)	Fe—N(1)—C(1)	114·3 (2)
O(3)—Fe—O(1)	103·7 (1)	O(5)—C(8)—C(7)	114·9 (2)
O(3)—Fe—O(7)	83·6 (1)	O(3)—C(6)—C(5)	116·0 (2)
O(9)—Fe—O(5)	73·2 (1)	O(7)—C(10)—C(9)	117·5 (2)
O(9)—Fe—O(3)	74·2 (1)	O(1)—C(4)—C(3)	117·2 (2)
O(9)—Fe—O(7)	106·2 (1)	C(8)—C(7)—N(2)	108·9 (2)
O(9)—Fe—O(1)	89·2 (1)	C(6)—C(5)—N(1)	109·5 (2)
N(2)—Fe—N(1)	73·5 (1)	C(10)—C(9)—N(2)	114·6 (2)
Fe—O(5)—C(8)	122·8 (2)	C(4)—C(3)—N(1)	112·7 (2)
Fe—O(3)—C(6)	120·8 (2)	N(2)—C(2)—C(1)	109·1 (2)
Fe—O(7)—C(10)	121·6 (2)	N(1)—C(1)—C(2)	109·5 (2)
Fe—O(1)—C(4)	120·6 (2)		

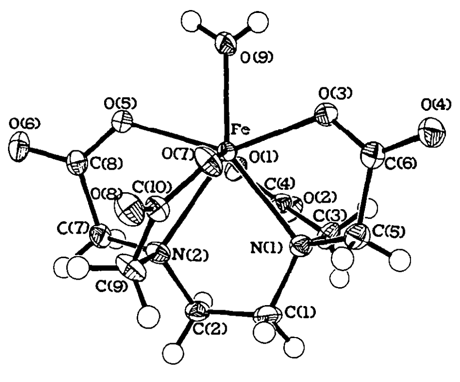

Fig. 1. The complex $[Fe(C_{10}H_{12}N_2O_8)(H_2O)]^-$ with atom designations. The thermal ellipsoids are shown at the 50% probability level. The hydrogen-atom radii are fixed at approximately 0·2 Å.

Discussion. The complex anions shown in Fig. 1 contain iron(III) atoms coordinated by four ionized carboxyl oxygen atoms and two nitrogen atoms from the hexadentate edta ligand and a seventh donor atom from a water molecule situated on the psuedo C_2 axis of the complex. The geometry is psuedo pentagonal bipyramidal as reported in the earlier study by Novozhilova, Polynova & Porai-Koshits (1975) but there are significant differences in many of the detailed bonding parameters. For the most part the bond lengths reported in the earlier study are shorter than those found here (Table 2) for corresponding atoms as might be expected from the fact that the unit-cell volume reported earlier was 7% smaller than that which we determine. Moreover, it is not clear that the x, y origin

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom positions and temperature factors, nonbonded distances, and a figure showing the possible hydrogen-bonding network and the sodium-ion coordination have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39236 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

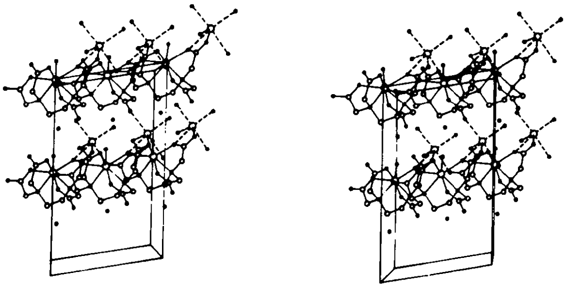

Fig. 2. Packing diagram for Na[Fe($C_{10}H_{12}N_2O_8$)(H_2O)].2H_2O as viewed down the *b* axis. The origin lies at the top back left corner with the *a* axis pointing to the right, the *b* axis projecting out of the plane, and the *c* axis pointing down. The dashed lines show the coordination about the sodium ions.

was fixed in the earlier study as the polar space group necessitates. The e.s.d.'s of the atom positions reported here are lower by an average factor of approximately 8×10^{-2}. With the more precise data, the apparent difference in C—C bond distances in the two types of glycinate rings (those containing a coordinating carboxyl oxygen in the equatorial plane of the pseudo pentagonal bipyramid and those containing a coordinated carboxyl oxygen axial to this plane) indicated in the earlier study disappears. On the other hand, these more precise data do indicate the same trend in Fe—O bond lengths and carboxyl C—O bond lengths observed by Hamor, Hamor & Hoard (1964) for Li[Fe($C_{10}H_{12}N_2O_8$)(H_2O)].H_2O. In that structure it was observed that as the Fe—O bond length increased, the C—O (coordinated) bond length decreased and the C—O (uncoordinated) bond length increased in the carboxylate groups. Fig. 2 presents a packing diagram for the structure.

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Bis{μ-[4-chloro-1,3-benzenedithiolato(2—)-*S*,*S*′]}-bis[diphenyltin(IV)], [$Sn_2(C_6H_3ClS_2)_2(C_6H_5)_4$]

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Abstract. $M_r = 895\cdot2$, monoclinic, $C2/c$, $a = 15\cdot886\,(6)$, $b = 7\cdot560\,(3)$, $c = 28\cdot883\,(9)$ Å, $\beta = 100\cdot93\,(5)°$, $U = 3406$ Å^3, $Z = 4$, $D_x = 1\cdot746$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot89$ mm^{-1}, $F(000) = 1760$, $T = 294\,(1)$ K, final $R = 0\cdot062$ for 1805 unique X-ray diffractometer data ($F_o > 3\sigma$) and 200 refined parameters. The title compound has been found to be dimeric. A twelve-membered ring is formed by two tetrahedrally bonded Sn atoms and two 4-chloro-1,3-benzenedithiolato moieties. The bond lengths conform with those of similar compounds; there are some differences in bond angles which may be ascribed to packing effects and intramolecular strains.

Introduction. Bis(1,2-dithiolato)tin(IV) and (1,2-dithiolato)diorganotin(IV) compounds have been known for several years, while the appropriate 1,3-dithiolates have been prepared by us only recently. For the diorganotin derivatives, *e.g.* for R_2Sn(tdt) ($R = CH_3$, C_6H_5; H_2tdt = 3,4-toluenedithiol) a monomeric structure was proposed (Epstein & Straub, 1965; Poller & Spillman, 1966), but it was also shown that tin

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