Crystal and Molecular Structure of Aquachlorobis(α-picolinato)iron(III)

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The crystal and molecular structure of the title compound has been determined from single-crystal *X*-ray data and refined by full-matrix least-squares to *R* 0.035. The yellow-green prismatic crystal of triclinic space group $P\bar{1}$ has unit cell dimensions: $a = 8.426(4)$, $b = 14.772(7)$, $c = 7.479(3)$ Å, $\alpha = 97.91(3)$, $\beta = 131.23(2)$, and $\gamma = 91.45(3)°$. The structure shows Fe^{III} co-ordinated octahedrally to a single carboxy-oxygen, the nitrogen of each of two picolinates, a chloride, and the oxygen of a water molecule.

RECENTLY, considerable interest has been shown in the utilization of iron(III)–oxo- and –hydroxo-species as model systems for the inorganic subunit in non-haem iron-containing proteins.[1–11] Two of the three types, [FeOFe]$^{4+}$ and [Fe$_3$O]$^{7+}$, have been characterized structurally,[10,12–14] but the third, particularly [Fe(μ-OH)$_2$-Fe]$^{4+}$, has yet to have its structure elucidated. Of the three types only the [Fe$_3$O]$^{9+}$ core has been obtained in the presence of simple amino-acids or peptides.

Schugar *et al.*[3] have discussed the preparation of both the monomeric [Fe(α-pic)$_2$Cl] (α-pic = α-picolinate), and the dimer. Both compounds are of importance with regard to model systems. The structure of the dimer is important in that it will provide an opportunity to delineate the bonding parameters in a di-hydroxo-bridged iron(III) species while the structure of the monomer will provide both a basis for comparison with the dimer and allow some insight into the relative efficiency of N *vs.* O co-ordination in the picolinate.

We report here the structure of [Fe(α-pic)$_2$Cl(H$_2$O)].

EXPERIMENTAL

Preparation of the Complex.—Single crystals were prepared by the procedure described in ref. 1. A solution of [FeCl$_3$]·6H$_2$O (0.1 mol), α-picolinic acid (0.02 mol), and urea (0.01 mol) in water (200 ml) were heated at 95 °C for 24 h. The yellowish green crystals which separated from the hot solution were washed with water and dried at 100 °C for 24 h. I.r. analyses indicated that the monomeric form had been obtained {Found: C, 40.85; H, 3.00; Cl, 10.35; Fe, 15.8; N, 7.8; O, 22.70. Calc. for [FeCl(C$_6$NO$_2$H$_4$)$_2$(H$_2$O)]: C, 40.75; H, 2.85; Cl, 10.05; Fe, 15.80; N, 7.93; O, 22.64%}.

Crystal Data.—[FeCl(C$_6$H$_4$NO$_2$)$_2$(H$_2$O)], $M = 351.293$, Triclinic, $a = 8.426(4)$, $b = 14.772(7)$, $c = 7.479(3)$ Å, $\alpha = 97.91(3)$, $\beta = 131.23(2)$, $\gamma = 91.45(3)$, $U = 691.56$ Å^3, $D_m = 1.764$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 1.687$. Space group $P\bar{1}$, no systematic absences. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 14.41 cm^{-1}.

Preliminary unit-cell and space-group data were obtained from Weissenberg and precession photographs. A crystal of dimensions 0.10 × 0.26 × 0.40 mm was mounted on a Picker four-circle automated diffractometer. Mo-K_α radiation was used for data collection. During alignment procedures, more accurate unit-cell dimensions were determined by least-squares fit of angular positions of 12 independent reflections. All independent reflections to sin $\theta_{max.}$ 0.643 were sampled by the θ–2θ scan procedure, the 2θ scan being 1° min^{-1} over a basic range of 2.6° extended to allow for a dispersion $\Delta\lambda/\lambda$ 0.592. Background measurements were made 20 s each on either side of the diffracted peak. The intensities of three standard reflections measured after every 40 reflections were relatively constant during data collection. Of the 4 407 measured reflections, 4 077 were classed as observed having $[|F_o|/\sigma(|F_o|)] > 1.5$, after subtraction of background and correction for Lorentz and polarization factors. No absorption corrections were made. The 3 004 highest-intensity reflections were used for structure-factor calculations.

Determination of the Structure.—The structure was determined by heavy-atom methods [15] and refined by full-matrix least-squares. A structure-factor calculation based on positions of the iron atom gave an initial *R* of 0.42. Two successive least-squares and difference-Fourier cycles allowed placement of all of the other non-hydrogen atoms and *R* was 0.095. Anomalous dispersion corrections were made for iron.[16] At this point anisotropic temperature factors were introduced for all atoms and several cycles of refinement lead to convergence with *R* 0.035. All changes in positional and thermal parameters were $<\sigma$ for the final cycle of refinement. A final difference-Fourier map showed no peaks above the expected background value. Hydrogen atoms were located but the positions were not refinable.

Final positional parameters are presented in Table 1, and bond distances and angles in Table 2. A projection of the molecular units is shown in Figure 1. Observed and calculated structure factors and temperature factors are listed in

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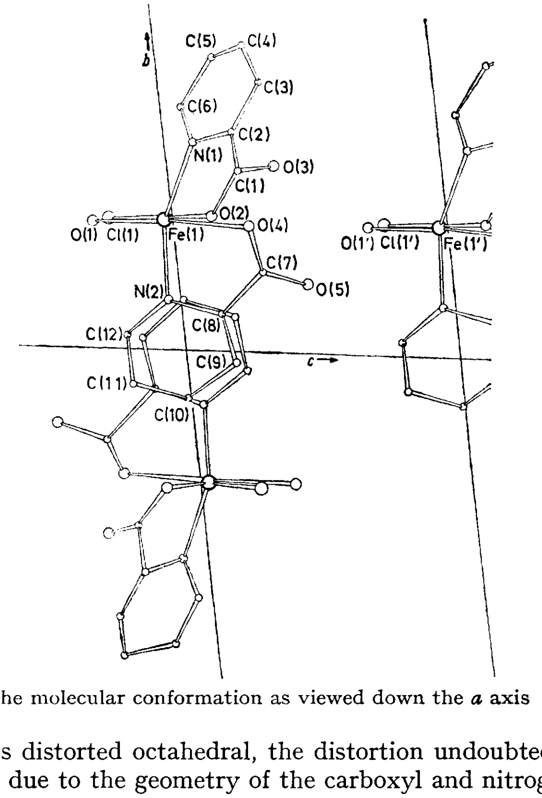
TABLE 1

Atomic co-ordinates, with estimated standard deviations in parentheses

	X/a	*Y/b*	*Z/c*
Fe(1)	0.253 06(6)	0.243 18(2)	−0.029 85(7)
Cl(1)	−0.101 3(1)	0.246 9(1)	−0.228 5(1)
O(1)	0.178 2(3)	0.239 4(1)	−0.352 4(3)
O(2)	0.565 1(3)	0.252 6(1)	0.133 7(4)
O(3)	−0.117 2(3)	0.345 5(1)	0.367 7(4)
O(4)	0.316 4(3)	0.231 2(1)	0.276 1(3)
O(5)	0.317 1(4)	0.132 6(1)	0.480 3(4)
N(1)	0.362 6(3)	0.389 8(1)	0.100 5(4)
N(2)	0.253 4(3)	0.096 9(1)	−0.044 3(4)
C(1)	0.687 7(4)	0.331 3(2)	0.251 8(4)
C(2)	0.575 3(4)	0.412 7(2)	0.239 8(5)
C(3)	0.684 0(5)	0.503 1(2)	0.363 2(6)
C(4)	0.562 3(6)	0.573 6(2)	0.334 7(7)
C(5)	0.340 1(6)	0.549 4(2)	0.181 5(8)
C(6)	0.244 2(5)	0.457 8(2)	0.066 2(7)
C(7)	0.306 5(4)	0.149 9(2)	0.315 0(4)
C(8)	0.276 4(4)	0.070 4(1)	0.136 8(4)
C(9)	0.275 3(4)	−0.021 6(2)	0.161 7(5)
C(10)	0.251 8(4)	−0.089 7(2)	−0.010 5(5)
C(11)	0.231 1(4)	−0.062 7(2)	−0.195 6(5)
C(12)	0.230 3(4)	0.031 2(2)	−0.210 1(4)

DISCUSSION

The unit cell contains two monomeric iron units. Each iron is co-ordinated to a chloride, the oxygen of a water molecule, and two α-picolinates. Each α-picolinate is bidentate, being co-ordinated through a carbonyl oxygen and the nitrogen. The geometry around each iron is distorted octahedral, the distortion undoubtedly being due to the geometry of the carboxyl and nitrogen co-ordination and to the relative bulk of the picolinate ligand.



The molecular conformation as viewed down the *a* axis

The monomeric units appear to be held together by hydrogen bonding. While the hydrogen atoms could be located, the positions did not refine satisfactorily and are not reported. The non-co-ordinated carboxy-oxygen atoms O(3) and O(5) are 2.69 and 2.628(2) Å from the oxygen of the co-ordinated water O(1′) one cell removed in the *Z* direction (Figure). These distances are reasonable for hydrogen-bonding interactions. The aromatic rings are stacked in parallel fashion perpendicular to the *x* direction of the cell.

TABLE 2

Interatomic angles (°) and distances (Å), with estimated standard deviations in parentheses

(*a*) Distances			
Fe(1)–Cl(1)	2.304(1)	O(3)–O(1′)	2.694(3)
Fe(1)–O(1)	2.043(2)	O(5)–O(1′)	2.628(2)
Fe(1)–N(1)	2.151(2)	Fe(1)–N(2)	2.150(2)
Fe(1)–O(2)	2.030(2)	Fe(1)–O(4)	2.015(2)
C(1)–O(2)	1.286(3)	C(7)–O(4)	1.286(3)
C(1)–O(3)	1.246(3)	C(7)–O(5)	1.243(3)
C(1)–C(2)	1.526(3)	C(7)–C(8)	1.526(3)
C(2)–N(1)	1.350(3)	C(8)–N(2)	1.352(3)
C(2)–C(3)	1.398(3)	C(8)–C(9)	1.398(3)
C(3)–C(4)	1.417(4)	C(9)–C(10)	1.416(4)
C(4)–C(5)	1.404(5)	C(10)–C(11)	1.394(4)
C(5)–C(6)	1.390(4)	C(11)–C(12)	1.406(3)
C(6)–N(1)	1.362(3)	C(12)–N(2)	1.363(3)
(*b*) Angles			
O(1)–Fe(1)–Cl(1)	88.74(6)	C(5)–C(4)–C(3)	118.47(25)
O(1)–Fe(1)–O(4)	173.48(7)	C(4)–C(3)–C(2)	117.78(28)
O(4)–Fe(1)–O(2)	93.10(8)	C(3)–C(2)–N(1)	122.73(24)
O(2)–Fe(1)–Cl(1)	173.88(11)	Fe(1)–N(2)–C(8)	112.65(15)
N(1)–Fe(1)–N(2)	160.15(8)	N(2)–C(8)–C(7)	114.19(19)
N(1)–Fe(1)–O(2)	77.33(7)	C(8)–C(7)–O(4)	115.26(20)
N(2)–Fe(1)–O(4)	78.29(7)	C(7)–O(4)–Fe(1)	119.02(15)
Fe(1)–N(1)–C(2)	113.48(14)	C(8)–C(7)–O(5)	119.34(21)
N(1)–C(2)–C(1)	114.09(19)	O(4)–C(7)–O(5)	125.40(22)
C(2)–C(1)–O(2)	114.66(21)	C(7)–C(8)–C(9)	122.53(22)
C(1)–O(2)–Fe(1)	119.91(15)	Fe(1)–N(2)–C(8)	112.65(14)
C(2)–C(1)–O(3)	119.32(22)	Fe(1)–N(2)–C(12)	128.53(16)
O(2)–C(1)–O(3)	126.01(23)	C(8)–N(2)–C(12)	118.81(19)
C(1)–C(2)–C(3)	122.73(24)	N(2)–C(12)–C(11)	121.48(23)
Fe(1)–N(1)–C(2)	113.48(14)	C(12)–C(11)–C(10)	119.38(23)
Fe(1)–N(1)–C(6)	127.29(19)	C(11)–C(10)–C(9)	119.28(22)
C(2)–N(1)–C(6)	119.16(21)	C(10)–C(9)–C(8)	117.77(24)
N(1)–C(6)–C(5)	121.05(29)	C(9)–C(8)–N(2)	123.27(21)
C(6)–C(5)–C(4)	120.25(27)		

The bond angles and distances in the α-picolinate are in agreement with those found in α-picoline itself.[17]

In chlorobis(*N*-n-propylsalicylaldiminato)iron(III),[18] the iron is five-co-ordinate, being co-ordinated to the nitrogen and oxygen atoms of each of two salicylaldiminato-ligands and a chloride. The iron–chloride distance [2.234 Å] is shorter than that [2.304(1) Å] determined here. The iron–nitrogen distance [2.096 Å] is somewhat shorter than those found for the picolinate ligand [2.151(2) and 2.150(2) Å].

The structure of an iron complex with proline is known in which iron forms a trimeric complex of the type $[Fe_3O]^{7+}$. In this structure the nitrogen is not co-ordinated.[19] Both the α-picolinate and the proline

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structure involve co-ordination of iron(III) to a ligand with a carboxy-group and a nitrogen present as part of a ring system. In the picoline system, nitrogen is part of an aromatic six-membered ring system where the ability of the nitrogen to co-ordinate to the metal is stabilized by the π-electron system. The pK_a of the carboxy-proton is 5.52. In the case of proline co-ordination such stabilization is not possible, the nitrogen being part of a five-membered saturated ring. The pK_a of the carboxy-proton is 2.00 and that of the nitrogen 10.60.

It has been stated that carboxylate co-ordination is favoured over nitrogen or sulphur co-ordination when all are available to iron.[20] The present structure would tend to cause reconsideration of this rule.

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