

**A Binuclear Chloroferrate Anion with Octahedral Metal Coordination: Octachloro( $\mu$ -oxalato)diferrate(III),  $[(\text{FeCl}_4)_2(\mu\text{-C}_2\text{O}_4)]^{4-}$**

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The results described here belong to our current investigations into the structure and thermal behavior of halometalates of  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$  with the nitrogen-containing heterocyclic base cations 1,4-dimethylpiperazinium, ( $\text{dmpipzH}_2$ ) $^{2+}$ , or triethylenediammonium, ( $\text{trienH}_2$ ) $^{2+}$ . $^{1,2}$  As has been previously observed with the zeolitic aluminophosphates $^3$  formed via precursors with analogous cations, the thermal treatment of such halometalates may produce phases exhibiting enhanced catalytic activity. Cavities or channels remaining in the solid residue after burning out of the organic component appear to be the reason for this activity, e.g. as recently described for several heterogeneous halogen exchange reactions on metal halides, as well as those on haloferrates or -aluminates. $^4$

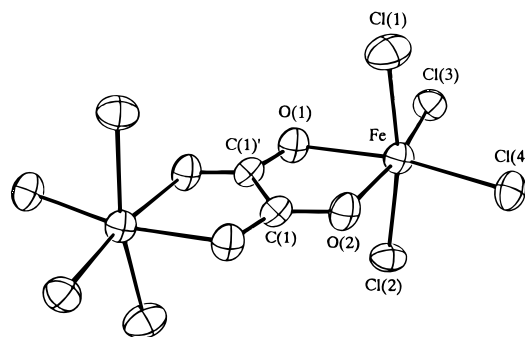
Well-formed yellow crystals of ( $\text{trienH}_2$ )[ $\text{FeCl}_4$ ] $\cdot 3\text{H}_2\text{O}$  were obtained from a hydrochloric acid solution containing equimolar amounts of trien and iron(II) chloride. This compound represents a simple analog to our previously described compounds $^{1,2}$  ( $\text{dmpipzH}_2$ )[ $\text{M}^{\text{II}}\text{X}_4$ ] ( $\text{M} = \text{Co}, \text{Zn}; \text{X} = \text{Cl}, \text{Br}$ ). EPR spectroscopy has established the presence of only Fe(II) in this compound. However, if the iron is introduced here as iron(II) oxalate instead of the chloride, the +2 oxidation state becomes unstable and undergoes air oxidation to form an iron(III) complex that precipitates as golden-yellow plates: ( $\text{trienH}_2$ ) $_2$ [( $\text{FeCl}_4$ ) $_2(\mu\text{-C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$ .

The most interesting feature of the crystal structure reported here is its discrete, centrosymmetric, binuclear anion in which two units  $\text{FeCl}_4$  are linked together by an oxalate group, resulting in the iron being octahedrally coordinated (Figure 1).

## Experimental Section

**Materials.** All reagents employed were commercially available high-grade purity substances (Merck and Aldrich chemicals), used as supplied without further purification. Elemental analyses were carried out using conventional methods of organic microanalysis (CHNS 932, Leco Corp., St. Joseph, MI) as well as gravimetry for the iron determination (compound decomposed in alkaline solution, boiled, dioxoxide filtered off, ignited at 600 °C, and weighed as  $\text{Fe}_2\text{O}_3$ ).

**Synthesis.** To a hot solution (70 °C) of 60 mmol (6.73 g) of triethylenediamine in 60 mL of 3 M HCl was added a solution of 60 mmol (10.87 g) of  $\text{Fe}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$  in 50 mL of 3 M HCl. The solution was stirred for several minutes and then cooled to room temperature for crystallization. Oxalic acid dihydrate first precipitates as colorless long prisms and was filtered off. Next, ( $\text{trienH}_2$ ) $_2$ [( $\text{FeCl}_4$ ) $_2(\mu\text{-C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$  crystallized as air-stable golden-yellow plates. Sometimes both compounds precipitate together, but after filtration and air-drying the different crystal types may be easily separated by hand. Recrystallization is from 3 M HCl. Anal. Calcd (found) for  $\text{C}_{14}\text{H}_{32}\text{N}_4\text{O}_6\text{Cl}_8\text{Fe}_2$  ( $\text{M} = 747.80 \text{ g}\cdot\text{mol}^{-1}$ ): C, 22.48 (21.8); H, 4.32 (4.4); N, 7.49 (6.7); Fe, 14.94 (15.2); Cl, 37.92 (37.5).



**Figure 1.** Structure of the anion  $[(\text{FeCl}_4)_2(\mu\text{-C}_2\text{O}_4)]^{4-}$ . Selected interatomic distances (Å): Fe–O(1) 2.120(2); Fe–O(2) 2.134(2); Fe–Cl(1) 2.3944(8); Fe–Cl(2) 2.3426(9); Fe–Cl(3) 2.2949(8); Fe–Cl(4) 2.304(1); C(1)–C(1') 1.538(4); O(1)–C(1') 1.254(3); O(2)–C(1) 1.244(3).

**Table 1.** Crystallographic Data for ( $\text{trienH}_2$ ) $_2$ [( $\text{FeCl}_4$ ) $_2(\mu\text{-C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}^a$

formula	$\text{C}_{14}\text{H}_{32}\text{N}_4\text{O}_6\text{Cl}_8\text{Fe}_2$	Z	1
fw	747.80	$d(\text{calc}), \text{g cm}^{-3}$	1.748
cryst syst	triclinic	abs coeff, $\text{mm}^{-1}$	1.810
space group	$P\bar{1}$	$\theta$ range, deg	2–26.5
$a, \text{Å}$	7.364(1)	no. of reflns colcd	2911
$b, \text{Å}$	9.038(2)	no. of obsd reflns	2686
$c, \text{Å}$	11.408(2)	(critn)	( $I > 2\sigma(I)$ )
$\alpha, \text{deg}$	78.37(3)	no. of params	219
$\beta, \text{deg}$	73.04(3)	$wR_2$	0.085
$\gamma, \text{deg}$	89.24(3)	$R_1$	0.033
$V, \text{Å}^3$	710.5(2)		

<sup>a</sup> The quantity minimized in the least squares procedure is  $\sum w(F_o^2 - F_c^2)^2$ ;  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$ .

**X-ray Crystallographic Study.** The data collection was performed at 293 K by the  $\theta/2\theta$ -scan method on a STADI-4 diffractometer (STOE & Cie., Darmstadt, Germany) using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ Å}$ ). Three standard reflections have been monitored after every 200 which revealed no significant crystal decay, and a  $\Psi$ -scan was carried out for empirical absorption correction. The structure was solved by direct methods (SHELXS-86) $^5$  and refined by full-matrix least-squares methods on  $F^2$  (SHELXL-93). $^6$  The non-hydrogen atoms were refined anisotropically; the hydrogen atoms, isotropically. Crystal data and some details on data collection and refinement are given in Table 1.

## Results and Discussion

In the structure of ( $\text{trienH}_2$ ) $_2$ [( $\text{FeCl}_4$ ) $_2(\mu\text{-C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$ , the anions occupy the corners of the unit cell. The cations ( $\text{trienH}_2$ ) $^{2+}$  are located between the anions, enabling the formation of bifurcated hydrogen bridges between the donor atom N(2) and the acceptor atoms Cl(3) and Cl(4) (Figure 2).

Three further types of hydrogen bonds which strengthen the Coulomb interactions between the anions and the cations exist in the structure. They are N–H $\cdots$ O; O–H $\cdots$ O, and C–H $\cdots$ Cl. The water molecule containing oxygen atom O(3) acts as acceptor for the donor group N(1)–H(1) being exactly directed to O(3). Furthermore, O(3) also acts as the H-donor atom in the weaker hydrogen bond to the oxygen atom O(1) of the oxalate group. Table 2 summarizes the pertinent interatomic distances and the bond angles for the hydrogen-bridging system.

The values in Table 2 indicate that the bifurcated hydrogen bridge between N(2) and Cl(3)/Cl(4) is nearly symmetrical. A second bifurcated hydrogen bridge is formed between O(3) and

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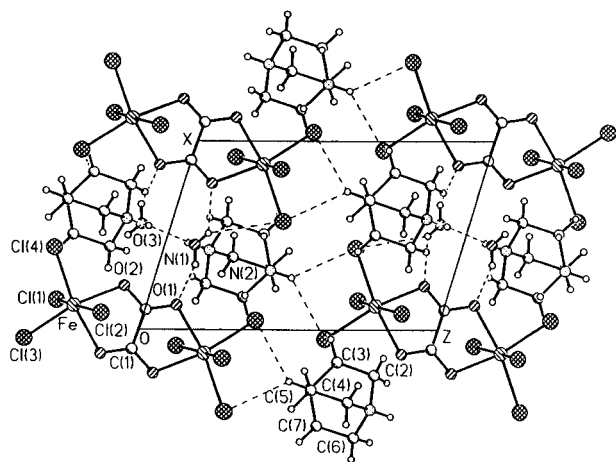
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**Figure 2.** Projection of the structure of  $(\text{trienH}_2)_2[(\text{FeCl}_4)(\mu\text{-C}_2\text{O}_4)] \cdot 2\text{H}_2\text{O}$  in the direction  $[010]$  (hydrogen bonds denoted by dotted lines).

**Table 2.** Interatomic Distances (Å) and bond angles (deg) for the System of Hydrogen Bridges

X-H...Y	d(X...Y)	d(H...Y)	$\omega$ (X-H...Y)
N(2)-H(2)...Cl(3)	3.276	2.60	138
N(2)-H(2)...Cl(4)	3.322	2.66	136
O(3)-H(16)...Cl(4)	3.475	2.85	148
O(3)-H(16)...O(2)	3.098	2.52	139
N(1)-H(1)...O(3)	2.703	1.85	168
O(3)-H(15)...O(1)	2.925	2.10	157
C(3)-H(6)...Cl(3)	3.434	2.84	158
C(7)-H(14)...Cl(4)	3.482	2.85	158

Cl(4)/O(2). Although the values for the relevant interatomic distances are near the limits for simple hydrogen bonds, this description of the hydrogen-bridging system is supported by the favoring geometrical situation in the structure. Furthermore, the participation of the second oxalato-oxygen atom O(2) at a hydrogen bond easily explains that the distances Fe—O(1) and Fe—O(2) are nearly equal. Therefore, the oxalate bridge in the

anion is relatively stiff. Accordingly, we also observe that the Fe—Cl bonds, being coplanar with the oxalate bridge, are nearly equidistant, whereas the slightly differentiated cis-positioned Fe—Cl bonds are clearly longer than the first ones and do not have any shortened distance to hydrogen atoms.

The anion  $[(\text{FeCl}_4)_2(\mu\text{-C}_2\text{O}_4)]^{4-}$  is the first example of an oxalato-bridged binuclear halometalate complex with metal cations in the oxidation state +3. Analogous anionic complexes of such a simple stoichiometry are hitherto known only for molybdenum(VI)<sup>7</sup> and titanium(IV)<sup>8</sup>:  $[(\text{MoO}_2\text{Cl}_2)_2(\mu\text{-C}_2\text{O}_4)]^{2-}$  and  $[(\text{TiF}_4)_2(\mu\text{-C}_2\text{O}_4)]^{2-}$ , respectively. On the other hand, there are numerous literature citations for a variety of oxalato-bridged molecules exhibiting more complicated structures, e.g. the neutral bis(allyl)chlororuthenium(IV) complex  $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})\text{-RuCl}]_2(\mu\text{-C}_2\text{O}_4)$ <sup>9</sup> or the oxo-chlorovanadium(IV) unit  $[\text{V}_2\text{O}_2\text{Cl}_2(\mu\text{-C}_2\text{O}_4)(\text{CH}_3\text{OH})_4]$ ,<sup>10</sup> both also being binuclear.

In  $[\{\text{W}^{\text{II}}\text{Br}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-C}_2\text{O}_4)]$ , the oxalate bridge accomplishes the heptacoordination of the tungsten atoms which in addition is formed by pairs of phosphine and carbonyl ligands, as well as by bromine.<sup>11</sup>

The geometry of the oxalate bridge in the molybdate anion  $[(\text{MoO}_2\text{Cl}_2)_2(\mu\text{-C}_2\text{O}_4)]^{2-}$  is nearly identical with that in the ferrate presented here. Only the distortion of the octahedra is stronger than in the iron complex: Cl(1)—Mo—Cl(2) = 159.8° compared with 169.7° for Cl(1)—Fe—Cl(2).

Further structural similarities exist between the anion  $[(\text{FeCl}_4)_2(\mu\text{-C}_2\text{O}_4)]^{4-}$  and the recently described bis( $\mu$ -fluoro)-bridged diaquafluorodiferrate(III) anion in  $(\text{Me}_4\text{N})_2[\text{Fe}_2\text{F}_8(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ <sup>12</sup> and, moreover, the neutral acetylacetonato complex  $(\text{acac})_2\text{Fe}(\mu\text{-C}_2\text{O}_4)\text{Fe}(\text{acac})_2 \cdot 0.5\text{H}_2\text{O}$ <sup>13</sup> in which iron(III) is only coordinated by oxygen.

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**Supporting Information Available:** Tables listing positional and thermal parameters and complete interatomic distances and bond angles (3 pages). Ordering information is given on any current masthead page.

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