

Table 2. Geometric parameters (Å, °)

(I)			
Cu...Cu ⁱ	2.657 (3)	Cu—N	2.176 (20)
Cu—O(1)	1.967 (10)	O(1)—C(1)	1.214 (26)
Cu—O(2)	1.979 (11)	O(2)—C(6)	1.249 (26)
Cu—O(3)	2.024 (11)	C(1)—O(4) ⁱ	1.235 (28)
Cu—O(4)	1.916 (11)	C(6)—O(3) ⁱ	1.313 (27)
(II)			
Cu...Cu ⁱⁱ	2.648 (5)	Cu—N	2.125 (13)
Cu—O(1)	1.972 (8)	O(1)—C(1)	1.273 (11)
Cu—O(2)	1.969 (8)	O(2)—C(5)	1.255 (7)
(I)			
N—Cu—O(1)	100.6 (6)	O(2)—Cu—O(4)	173.0 (5)
N—Cu—O(2)	92.3 (6)	O(3)—Cu—O(4)	90.7 (4)
N—Cu—O(3)	96.4 (6)	O(1)—C(1)—O(4) ⁱ	128.4 (16)
N—Cu—O(4)	94.8 (6)	O(2)—C(6)—O(3) ⁱ	127.8 (15)
O(1)—Cu—O(2)	89.9 (4)	Cu—O(1)—C(1)	123.3 (13)
O(1)—Cu—O(3)	163.0 (4)	Cu—O(2)—C(6)	118.6 (14)
O(1)—Cu—O(4)	89.0 (4)	Cu—O(3)—C(6) ⁱ	122.9 (12)
O(2)—Cu—O(3)	88.4 (4)	Cu—O(4)—C(1) ⁱ	121.4 (13)
(II)			
N—Cu—O(1)	95.8 (4)	O(2)—Cu—O(2) ⁱⁱⁱ	168.3 (4)
N—Cu—O(2)	95.9 (4)	O(1)—C(1)—O(1) ⁱⁱ	124.1 (11)
O(1)—Cu—O(2)	92.5 (3)	O(2)—C(5)—O(2) ⁱⁱ	127.1 (8)
O(1)—Cu—O(1) ⁱⁱⁱ	168.5 (4)	Cu—O(1)—C(1)	123.5 (5)
O(1)—Cu—O(2) ⁱⁱⁱ	86.3 (3)	Cu—O(2)—C(5)	122.3 (7)

Symmetry codes: (i) $y, x, -z$; (ii) $1 - x + y, y, z$; (iii) $x - y, -y, 1 - z$.

Compound (I): The density was measured by flotation in a tetrabromoethane-cyclohexane mixture. The specimen was coated with adhesive to prevent efflorescence. Laue group $\bar{3}m1$ and systematic absences, $00l$ for $l \neq 3n$, indicated an enantiomorphic pair of the space groups $P3_121$ (No. 152) and $P3_221$ (No. 154). Assuming the space group to be $P3_121$, the structure was solved based on the Patterson function using *SHELXS86* (Sheldrick, 1986). The benzene molecule could not be located on difference syntheses. The enantiomorphic space group $P3_221$ gave almost the same R factor. The large R value may be due to the disorder of the benzene molecule, which was not taken into account in the refinement. The B_{eq} values for the methyl C atoms (9.2–22.5 Å) are abnormally large, suggesting disorder. The bond lengths and angles involving the $C(CH_3)_3$ groups were obtained with low accuracy. The structure was refined using *UNICSIII* (Sakurai & Kobayashi, 1979) on a FACOM M-780/10 computer at Keio University.

Compound (II): The density was measured by flotation in a tetrabromoethane-cyclohexane mixture. The intensities of five standard reflections decayed by 20%; this was corrected for. Laue group $\bar{3}m1$ and systematic absences, hkl for $-h+k+l \neq 3n$, indicated the space group $R32$ (No. 155), $R3m$ (No. 160) or $R\bar{3}m$ (No. 166). At first, the structure was solved in $R32$. The positions of the Cu atoms on the twofold axis were obtained by direct methods and those of the other non-H atoms by Fourier syntheses. The R value was reduced to 0.072 by introducing the anisotropic thermal parameters. At this stage of the refinement, crystallographic mirror symmetry of the binuclear complex was expected. The space group was then changed to $R\bar{3}m$ to reduce the number of independent non-H atoms from 26 to 16. The refinement gave the same residual factor $R = 0.072$ with normal bond lengths and reasonable thermal parameters. The benzene molecule could not be located on the difference syntheses. The large R value may be due to the disorder of the benzene molecule. The structure was solved using *SHELXS86* and refined using *UNICSIII* with all calculations being performed on a FACOM M-780/10 computer at Keio University.

This work was supported by the Kurata research grant to one of the authors (SO).

Lists of structure factors, anisotropic thermal parameters, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55490 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1018]

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FeCl₃ Behavior in Acetonitrile: Structures of [FeCl₂(CH₃CN)₄][FeCl₄] and [AlCl(CH₃CN)₅][FeCl₄]₂·CH₃CN

Y. GAO, J. GUERY AND C. JACOBONI

Laboratoire des Fluorures - URA 449, Faculté des Sciences, Université du Maine, 72017 Le Mans CEDEX, France

(Received 10 March 1992; accepted 23 September 1992)

Abstract

The structures of the complexes [FeCl₂(CH₃CN)₄][FeCl₄], tetrakis(acetonitrile)dichloroiron(III) tetrachloroferrate(1-), and [AlCl(CH₃CN)₅][FeCl₄]₂·CH₃CN, pentakis(acetonitrile)chloroaluminium(III) bis[tetrachloroferrate(1-)] acetonitrile solvate, have been determined from single-crystal X-ray diffraction data. [FeCl₂(CH₃CN)₄][FeCl₄] is built up from [FeCl₂(CH₃CN)₄]⁺ octahedra and [FeCl₄]⁻ tetrahedra whereas [AlCl(CH₃CN)₅][FeCl₄]₂·CH₃CN is composed of [AlCl(CH₃CN)₅]²⁺ octahedra, [FeCl₄]⁻ tetrahedra and uncoordinated CH₃CN molecules.

Comment

Very pure starting fluorides are required for fluoride glasses of high optical performance (France, Carter,

Moore & Williams, 1987); new ways of synthesizing such pure fluorides have been sought for several years (Folweiler & Pink, 1987; Guery & Jacoboni, 1988). A previous study of the behavior of zirconium chloride in acetonitrile led to the determination of the crystal structure of $ZrCl_4 \cdot 2CH_3CN$ (Guery, Leblanc & Jacoboni, 1989). The decreasing content of 3d transition metals (especially iron) during the crystallization process was explained by the formation of more soluble complexes. There have been few studies into the behavior of iron trichloride in acetonitrile (Hathaway & Holah, 1964; Constant, Daran & Jeannin, 1973) but $AlCl_3$ -acetonitrile complexes have been studied extensively (Dalibart, Fouassier & Forel, 1977; Akitt & Duncan, 1977; Lancelin, Dubois & Vandorpe, 1979; Dalibart, Derouault & Forel, 1980) and the crystal structure of $[AlCl(CH_3CN)_5][AlCl_4] \cdot 2CH_3CN$ has been determined (Howard, Smart & Gilmore, 1976; Beattie, Jones, Howard, Smart, Gilmore & Akitt, 1979). The primary aim of the present work was to study the structure of iron trichloride-acetonitrile complexes and to compare it with the those of aluminium and zirconium complexes.

Many arrangements of $[Fe^{III}Cl_xS_{6-x}]$ octahedra (S = solvent) have been reported or inferred from spectroscopic studies of solutions and the $[Fe^{III}Cl_2S_4]$ configuration in the $[FeCl_2(dmsO)_4][FeCl_4]$ complex is known following a full X-ray structure determination (Bennet, Cotton & Weaver, 1967). A comparison of the $[FeCl_2(CH_3CN)_4]^+$ and $[FeCl_2(dmsO)_4]^+$ octahedra in the $[FeCl_2(CH_3CN)_4][FeCl_4]$ and $[FeCl_2(dmsO)_4][FeCl_4]$ complexes shows that the chloride ions are *cis* in the former but *trans* in the latter; this difference in configuration could be due to the larger size of the dmsO ligand. Table 2 shows that the formation of coordination bonds between the octahedrally coordinated cation

and acetonitrile molecules leads to longer C—C distances but that C—N distances do not vary significantly in the various CH_3CN coordination schemes. These results confirm the tendency for Fe^{3+} ions to adopt a tetrahedral coordination in a chloride medium as in the case of $[Fe^{II}(CH_3CN)_6][Fe^{III}Cl_4]_2$ (Stork-Blaise, Verschoor & Romers, 1972). Furthermore $MCl_n \cdot 2CH_3CN$ ($M = Zr, Fe, Al$) seems to be the most stable phase in the crystalline state, despite the fact that various species have been described in acetonitrile solvated chlorides (Constant, Daran & Jeannin 1973; Dalibart, Fouassier & Forel, 1977). The main feature of the crystal chemistry of such complexes is the combination of $[MCl_4]^-$ tetrahedra with $[MCl_x(CH_3CN)_{6-x}]^{(n-x)+}$ octahedra of variable composition and the participation of free acetonitrile molecules to accommodate the $MCl_n \cdot 2CH_3CN$ stoichiometry in the solid state.

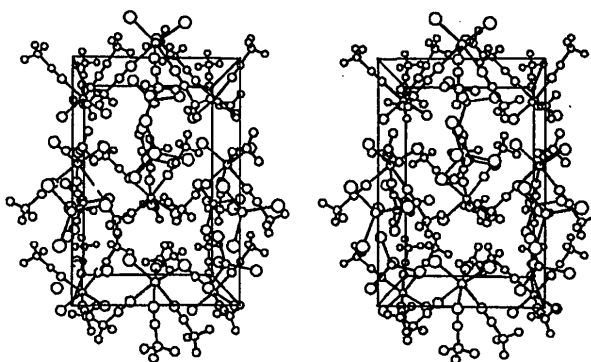


Fig. 2. Stereoscopic view of $[FeCl_2(CH_3CN)_4][FeCl_4]$; the b axis is vertical and the c axis horizontal.

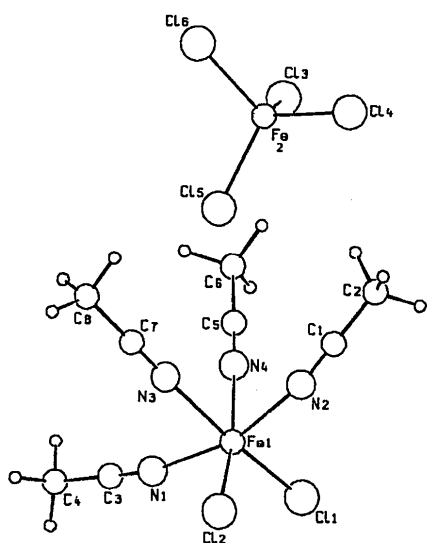


Fig. 1. View of the non-H atoms of $[FeCl_2(CH_3CN)_4][FeCl_4]$ showing the atomic numbering scheme used.

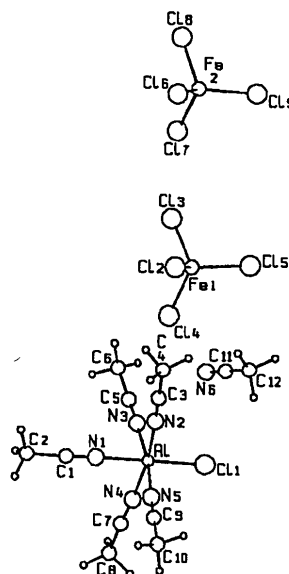


Fig. 3. View of the non-H atoms of $[AlCl(CH_3CN)_5][FeCl_4] \cdot 2CH_3CN$ showing the atomic numbering scheme used.

Experimental**[FeCl₂(CH₃CN)₄][FeCl₄]***Crystal data* $M_r = 488.62$

Orthorhombic

 $Pna2_1$ $a = 13.467 (1) \text{ \AA}$ $b = 14.879 (1) \text{ \AA}$ $c = 10.1125 (8) \text{ \AA}$ $V = 2026.29 \text{ \AA}^3$ $Z = 4$ $D_x = 1.602 \text{ Mg m}^{-3}$ *Data collection*Stoe-Siemens AED-2
diffractometer $\theta/2\theta$ scans

Absorption correction:

Gaussian (SHELX76;
Sheldrick, 1976) $T_{\min} = 0.4351$, $T_{\max} =$
0.7123

6069 measured reflections

4297 independent reflections

*Refinement*Refinement on F Final $R = 0.035$ $wR = 0.035$ $S = 1.38$

1639 reflections

193 parameters

All H-atom parameters re-
fined

Unit weights applied

 $(\Delta/\sigma)_{\max} = 0.012$ **[AlCl(CH₃CN)₅][FeCl₄]₂·CH₃CN***Crystal data* $M_r = 703.75$

Orthorhombic

 $P2_12_12_1$ $a = 10.1025 (5) \text{ \AA}$ $b = 14.513 (1) \text{ \AA}$ $c = 21.032 (2) \text{ \AA}$ $V = 3083.69 \text{ \AA}^3$ $Z = 4$ $D_x = 1.516 \text{ Mg m}^{-3}$ *Data collection*Stoe-Siemens AED-2
diffractometer $\theta/2\theta$ scans

Absorption correction:

Gaussian (SHELX76)

 $T_{\min} = 0.4465$, $T_{\max} =$
0.5932

4057 measured reflections

3325 independent reflections

Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$ Cell parameters from 36
reflections $\theta = 15-16^\circ$ $\mu = 22.14 \text{ mm}^{-1}$ $T = 293 \text{ K}$

Needle

 $0.38 \times 0.27 \times 0.27 \text{ mm}$

Red

1639 observed reflections

 $[I > 3.0\sigma(I)]$ $R_{\text{int}} = 0.01$ $\theta_{\max} = 30^\circ$ $h = -4 \rightarrow 20$ $k = 0 \rightarrow 23$ $l = -16 \rightarrow 16$

3 standard reflections

frequency: 60 min

intensity variation: 22.5%

 $\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*for *X-ray Crystallogra-*
phy (1974, Vol. IV, Table
2.2B) (Fe, Cl) and Cromer
& Mann (1968) (C, H, N)*Refinement*Refinement on F Final $R = 0.042$ $wR = 0.042$ $S = 2.21$

1674 reflections

290 parameters

All H-atom parameters re-
fined

Unit weights applied

 $(\Delta/\sigma)_{\max} = 0.014$ For both compounds: Data collection: *DIF4*. Cell refinement:*DIF4*. Data reduction: *REDU4*. Program(s) used to solve struc-ture: *SHELX76* (option *TANG*). Program(s) used to refine struc-ture: *SHELX76*. Molecular graphics: *SCHAKAL*. $\Delta\rho_{\max} = 0.296 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.432 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*for *X-ray Crystallogra-**phy* (1974, Vol. IV, Table

2.2B) (Fe, Al, Cl) and

Cromer & Mann (1968)

(C, H, N)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
[FeCl ₂ (CH ₃ CN) ₄][FeCl ₄]				
Fe(1)	0.6065 (1)	0.4217 (1)	0.5	0.0453 (5)
Fe(2)	0.5600 (1)	0.8814 (1)	0.5002 (2)	0.0473 (5)
Cl(1)	0.5523 (3)	0.3456 (2)	0.6730 (3)	0.072 (2)
Cl(2)	0.5635 (3)	0.3249 (2)	0.3397 (3)	0.073 (2)
Cl(3)	0.6074 (2)	0.9072 (2)	0.7000 (3)	0.084 (2)
Cl(4)	0.3990 (2)	0.8888 (2)	0.4810 (5)	0.093 (2)
Cl(5)	0.6125 (2)	0.7488 (2)	0.4375 (3)	0.078 (2)
Cl(6)	0.6291 (2)	0.9835 (2)	0.3723 (3)	0.088 (2)
N(1)	0.7554 (5)	0.3788 (4)	0.515 (1)	0.065 (5)
N(2)	0.4794 (5)	0.5044 (4)	0.484 (1)	0.059 (4)
N(3)	0.6663 (6)	0.5119 (6)	0.3479 (8)	0.053 (5)
N(4)	0.6565 (7)	0.5299 (6)	0.6238 (8)	0.054 (5)
C(1)	0.4244 (5)	0.5621 (5)	0.489 (1)	0.052 (4)
C(3)	0.8381 (7)	0.3708 (5)	0.5330 (9)	0.058 (6)
C(5)	0.6825 (7)	0.5896 (6)	0.6844 (1)	0.053 (5)
C(7)	0.6983 (7)	0.5597 (6)	0.2755 (9)	0.050 (2)
C(2)	0.3547 (6)	0.6359 (5)	0.497 (2)	0.067 (5)
C(4)	0.9449 (6)	0.3616 (7)	0.553 (1)	0.074 (7)
C(6)	0.7170 (9)	0.6680 (7)	0.760 (1)	0.079 (7)
C(8)	0.741 (1)	0.6230 (8)	0.179 (1)	0.084 (8)
[AlCl(CH ₃ CN) ₅][FeCl ₄] ₂ ·CH ₃ CN				
Fe(1)	0.4921 (2)	0.4293 (2)	0.5026 (1)	0.067 (1)
Fe(2)	0.4934 (2)	0.4322 (2)	0.8438 (1)	0.068 (1)
Al	0.6252 (3)	0.3778 (2)	0.1640 (2)	0.040 (2)
Cl(1)	0.4141 (3)	0.3438 (2)	0.1602 (2)	0.059 (2)
Cl(2)	0.5602 (4)	0.5723 (3)	0.5025 (2)	0.081 (2)
Cl(3)	0.5712 (5)	0.3621 (3)	0.5866 (2)	0.105 (3)
Cl(4)	0.5679 (5)	0.3643 (3)	0.4175 (2)	0.101 (3)
Cl(5)	0.2783 (4)	0.4258 (5)	0.5092 (2)	0.109 (4)
Cl(6)	0.5761 (4)	0.5692 (3)	0.8336 (2)	0.085 (2)
Cl(7)	0.5638 (5)	0.3453 (4)	0.7671 (2)	0.129 (4)
Cl(8)	0.5602 (5)	0.3755 (4)	0.9330 (2)	0.117 (4)
Cl(9)	0.2796 (3)	0.4377 (3)	0.8383 (2)	0.077 (3)
N(1)	0.8184 (8)	0.4044 (7)	0.1669 (5)	0.047 (6)
N(2)	0.607 (1)	0.4676 (7)	0.2342 (4)	0.047 (6)
N(3)	0.667 (1)	0.2844 (7)	0.2291 (4)	0.047 (6)
N(4)	0.673 (1)	0.2914 (7)	0.0947 (4)	0.045 (6)
N(5)	0.612 (1)	0.4775 (7)	0.1008 (4)	0.043 (6)
N(6)	0.416 (1)	0.1804 (8)	0.3214 (6)	0.076 (8)
C(1)	0.928 (1)	0.4139 (9)	0.1671 (6)	0.055 (8)
C(3)	0.600 (1)	0.5188 (9)	0.2744 (5)	0.048 (8)
C(5)	0.699 (1)	0.2392 (9)	0.2693 (6)	0.049 (9)
C(7)	0.711 (1)	0.2485 (9)	0.0519 (5)	0.048 (8)
C(9)	0.602 (1)	0.5345 (8)	0.0656 (5)	0.047 (7)
C(11)	0.347 (1)	0.2394 (9)	0.3241 (7)	0.060 (9)
C(2)	1.074 (1)	0.423 (1)	0.1695 (8)	0.074 (9)
C(4)	0.591 (1)	0.5862 (8)	0.3237 (6)	0.061 (8)
C(6)	0.740 (2)	0.183 (1)	0.3235 (7)	0.08 (1)

C(8)	0.748 (1)	0.197 (1)	0.0003 (6)	0.07 (1)	N(5)—Al—N(3)	171.0 (5)	N(3)—C(5)—C(6)	178 (1)
C(10)	0.588 (2)	0.611 (1)	0.0201 (6)	0.07 (1)	N(5)—Al—N(2)	90.7 (4)	N(4)—C(7)—C(8)	176 (1)
C(12)	0.263 (2)	0.316 (1)	0.3281 (8)	0.08 (1)	N(5)—Al—N(4)	89.2 (4)	N(5)—C(9)—C(10)	179 (1)
					N(5)—Al—N(1)	86.9 (4)	N(6)—C(11)—C(12)	178 (2)
					N(5)—Al—C(11)	94.3 (3)		

Table 2. Bond distances (Å) and angles (°)

[FeCl ₂ (CH ₃ CN) ₄][FeCl ₄]			
Fe(1)—N(1)	2.109 (7)	Cl(3)—Cl(5)	3.551 (5)
Fe(1)—N(2)	2.114 (6)	Cl(3)—Cl(4)	3.585 (5)
Fe(1)—N(4)	2.149 (8)	Cl(4)—Cl(6)	3.577 (4)
Fe(1)—N(3)	2.195 (8)	Cl(4)—Cl(5)	3.578 (4)
Fe(1)—Cl(1)	2.207 (3)	Cl(5)—Cl(6)	3.561 (4)
Fe(1)—Cl(2)	2.244 (3)	N(1)—N(4)	2.84 (1)
Fe(2)—Cl(3)	2.154 (3)	N(1)—N(3)	2.86 (1)
Fe(2)—Cl(4)	2.179 (2)	N(2)—N(4)	2.80 (1)
Fe(2)—Cl(5)	2.190 (3)	N(2)—N(3)	2.87 (1)
Fe(2)—Cl(6)	2.202 (4)	N(3)—N(4)	2.81 (1)
Cl(1)—N(4)	3.121 (9)	N(1)—C(3)	1.14 (1)
Cl(1)—N(2)	3.194 (9)	N(2)—C(1)	1.13 (1)
Cl(1)—N(1)	3.208 (9)	N(3)—C(7)	1.11 (1)
Cl(1)—Cl(2)	3.388 (5)	N(4)—C(5)	1.13 (1)
Cl(2)—N(3)	3.109 (9)	Cl(1)—C(2)	1.45 (1)
Cl(2)—N(1)	3.232 (9)	C(3)—C(4)	1.46 (1)
Cl(2)—N(2)	3.247 (8)	C(5)—C(6)	1.47 (1)
Cl(3)—Cl(6)	3.516 (5)	C(7)—C(8)	1.47 (2)
N(1)—Fe(1)—N(2)	161.9 (3)	N(3)—Fe(1)—Cl(2)	88.9 (2)
N(1)—Fe(1)—N(4)	83.6 (3)	Cl(1)—Fe(1)—Cl(2)	99.1 (1)
N(1)—Fe(1)—N(3)	83.4 (3)	Cl(3)—Fe(2)—Cl(4)	111.7 (2)
N(1)—Fe(1)—Cl(1)	96.0 (3)	Cl(3)—Fe(2)—Cl(5)	109.7 (1)
N(1)—Fe(1)—Cl(2)	95.8 (3)	Cl(3)—Fe(2)—Cl(6)	107.6 (1)
N(2)—Fe(1)—N(4)	82.1 (3)	Cl(4)—Fe(2)—Cl(5)	110.0 (1)
N(2)—Fe(1)—N(3)	83.5 (3)	Cl(4)—Fe(2)—Cl(6)	109.5 (1)
N(2)—Fe(1)—Cl(1)	95.3 (3)	Cl(5)—Fe(2)—Cl(6)	108.3 (1)
N(2)—Fe(1)—Cl(2)	96.3 (3)	N(4)—C(5)—C(6)	178 (1)
N(4)—Fe(1)—N(3)	80.5 (3)	N(1)—C(3)—C(4)	178 (1)
N(4)—Fe(1)—Cl(1)	91.5 (2)	N(2)—C(1)—C(2)	179 (1)
N(4)—Fe(1)—Cl(2)	169.4 (2)	N(3)—C(7)—C(8)	180 (1)
N(3)—Fe(1)—Cl(1)	172.0 (2)		
[AlCl(CH ₃ CN) ₅][FeCl ₄] ₂ .CH ₃ CN			
Fe(1)—Cl(4)	2.163 (5)	Cl(6)—Cl(7)	3.539 (7)
Fe(1)—Cl(5)	2.165 (5)	Cl(6)—Cl(9)	3.553 (5)
Fe(1)—Cl(3)	2.171 (5)	Cl(7)—Cl(9)	3.504 (6)
Fe(1)—Cl(2)	2.187 (5)	Cl(7)—Cl(8)	3.518 (6)
Fe(2)—Cl(8)	2.158 (5)	Cl(8)—Cl(9)	3.581 (6)
Fe(2)—Cl(9)	2.165 (4)	N(1)—N(2)	2.72 (1)
Fe(2)—Cl(7)	2.167 (6)	N(1)—N(3)	2.66 (1)
Fe(2)—Cl(6)	2.167 (5)	N(1)—N(4)	2.68 (1)
Al—N(5)	1.969 (9)	N(1)—N(5)	2.72 (1)
Al—N(3)	1.97 (1)	N(2)—N(3)	2.73 (1)
Al—N(2)	1.98 (1)	N(2)—N(5)	2.81 (1)
Al—N(4)	1.98 (1)	N(3)—N(4)	2.83 (1)
Al—N(1)	1.991 (9)	N(4)—N(5)	2.77 (1)
Al—Cl(1)	2.190 (4)	N(1)—C(1)	1.11 (2)
Cl(1)—N(4)	3.05 (1)	N(2)—C(3)	1.13 (1)
Cl(1)—N(5)	3.05 (1)	N(3)—C(5)	1.12 (2)
Cl(1)—N(3)	3.06 (1)	N(4)—C(7)	1.16 (1)
Cl(1)—N(2)	3.07 (1)	N(5)—C(9)	1.12 (1)
Cl(2)—Cl(4)	3.511 (6)	N(6)—C(11)	1.11 (2)
Cl(2)—Cl(3)	3.528 (6)	C(1)—C(2)	1.48 (2)
Cl(2)—Cl(5)	3.557 (7)	C(3)—C(4)	1.43 (2)
Cl(3)—Cl(5)	3.501 (6)	C(5)—C(6)	1.46 (2)
Cl(3)—Cl(4)	3.557 (6)	C(7)—C(8)	1.38 (2)
Cl(4)—Cl(5)	3.616 (7)	C(9)—C(10)	1.47 (2)
Cl(6)—Cl(8)	3.507 (6)	C(11)—C(12)	1.40 (2)
Cl(4)—Fe(1)—Cl(5)	113.4 (2)	N(3)—Al—N(2)	87.4 (4)
Cl(4)—Fe(1)—Cl(3)	110.3 (2)	N(3)—Al—N(4)	91.3 (4)
Cl(4)—Fe(1)—Cl(2)	107.6 (2)	N(3)—Al—N(1)	84.3 (4)
Cl(5)—Fe(1)—Cl(3)	107.7 (2)	N(3)—Al—C(11)	94.6 (3)
Cl(5)—Fe(1)—Cl(2)	109.6 (2)	N(2)—Al—N(4)	171.3 (5)
Cl(3)—Fe(1)—Cl(2)	108.1 (2)	N(2)—Al—N(1)	86.6 (4)
Cl(8)—Fe(2)—Cl(9)	111.9 (2)	N(2)—Al—Cl(1)	94.9 (3)
Cl(8)—Fe(2)—Cl(7)	108.9 (2)	N(4)—Al—N(1)	87.4 (4)
Cl(8)—Fe(2)—Cl(6)	108.4 (2)	N(4)—Al—Cl(1)	93.8 (3)
Cl(9)—Fe(2)—Cl(7)	108.0 (2)	N(1)—Al—Cl(1)	178.1 (3)
Cl(9)—Fe(2)—Cl(6)	110.2 (2)	N(1)—C(1)—C(2)	177 (1)
Cl(7)—Fe(2)—Cl(6)	109.5 (2)	N(2)—C(3)—C(4)	178 (1)

Anhydrous FeCl₃ (and/or AlCl₃) were dissolved until saturation in 0.2 μm filtered CH₃CN which had been distilled twice and kept on molecular sieves. The [FeCl₂(CH₃CN)₄][FeCl₄] (red) and [AlCl(CH₃CN)₅][FeCl₄]₂.CH₃CN (green) crystals were formed after slow evaporation (3 d) of the solvent at room temperature. As such complexes have a very high hygroscopicity, all work was performed inside a dry glove box (<5 p.p.m. H₂O). Magnetic susceptibility measurements at 80–295 K showed that [FeCl₂(CH₃CN)₄][FeCl₄] exhibits a true paramagnetic behavior and gave the expected value (5.92 μB mol⁻¹) for the Curie constant of Fe³⁺ in its high-spin configuration. For the X-ray structure investigations, small crystals were sealed inside 0.3 mm diameter Lindemann tubes.

[FeCl₂(CH₃CN)₄][FeCl₄] crystallizes in the orthorhombic system with systematic absences suggesting the space groups *Pnma* or *Pna2*₁. The cell parameters are consistent with those cited by Constant, Daran & Jeannin (1973) for the complex they had obtained from FeCl₃ in acetonitrile (formula and crystal structure not determined). Starting with the centrosymmetric space group *Pnma*, direct methods (*SHELX76 EEES*) located the Fe atoms but refinement and Fourier mapping did not reveal the remaining atoms. With the same starting set of Fe atoms and the non-centrosymmetric space group *Pna2*₁, all but the H atoms were found quickly. The refinement of the structure with anisotropic thermal parameters gave *R* = 0.04 at this stage. Subsequent refinement with the H atoms fixed in CH₃ groups by restricting their positions (*SHELX76 AFIX*) and anisotropic thermal parameters for all non-H atoms gave *R* = 0.035 and *wR* = 0.035. The refined atomic parameters are listed in Table 1 and main bond distances and angles in Table 2. The labeled diagram of [FeCl₂(CH₃CN)₄][FeCl₄] in Fig. 1 shows that [FeCl₂(CH₃CN)₄][FeCl₄] is built up from [FeCl₄]⁻ tetrahedra and [FeCl₂(CH₃CN)₄]⁺ octahedra; the octahedra have two chloride ions in *cis* positions and four acetonitrile molecules as other ligands. Table 2 shows that the Fe—N distances are clearly shorter than those of Fe—Cl, leading to severe distortion of the [FeCl₂(CH₃CN)₄]⁺ polyhedron. Although the mean Fe—Cl distances (⟨Fe—Cl⟩ = 2.181 Å, *σ_n* = 0.013) in the [FeCl₄]⁻ tetrahedra are consistent with those found in previous studies (Bennet, Cotton, & Weaver, 1967; Stork-Blaisse, Verschoor & Romers, 1972), the large standard deviation also shows that the tetrahedron is far from regular. Fig. 2 shows the 'hydrogen bonding' between Cl atoms and the neighboring CH₃ groups.

The existence of two different sites for Fe in [FeCl₂(CH₃CN)₄][FeCl₄] prompted us to replace half of the Fe content by Al to look at possible order between the two trivalent cations in this new structure; small green crystals are obtained with composition [AlCl(CH₃CN)₅][FeCl]₂.CH₃CN. The refined atomic parameters are given in Table 1, main bond distances and angles in Table 2 and Fig. 3 shows the atom labeling of [AlCl(CH₃CN)₅][FeCl₄]₂.CH₃CN. Owing to the rapid decrease of the intensities as 2θ increases and the degradation of the crystal under X-ray conditions, the ratio of the number of observed reflections is only 5.7 leading to a low-accuracy determination of the crystal structure. The structure of [AlCl(CH₃CN)₅][FeCl₄]₂.CH₃CN is identical to that of [AlCl(CH₃CN)₅][AlCl₄]₂.CH₃CN being built from [FeCl₄]⁻

tetrahedra, $[\text{AlCl}(\text{CH}_3\text{CN})_5]^{2+}$ octahedra and isolated CH_3CN molecules.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55614 (61 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1009]

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Structures of Perfragilin A and B

SAFIA KHALIL RIZVI, M. B. HOSSAIN AND
D. VAN DER HELM

Department of Chemistry and Biochemistry,
Oklahoma University, Norman, Oklahoma 73019, USA

(Received 9 March 1992; accepted 11 August 1992)

Abstract

The two perfragilins both have a similar backbone (an isoquinolinetrione skeleton) but differ in their

substitution pattern at C(6) and C(7); perfragilin A has a thiomethyl group at C(6) and amide group at C(7), whereas perfragilin B has a thiomethyl group at both these positions. The effects of these substituents are reflected in the bond distances and bond angles, particularly in the benzoquinone segments of the molecules. The amide group in perfragilin A leads to a resonance structure and a planar isoquinoline ring system [r.m.s. deviation 0.026 (2) Å]. The presence of the two thiomethyl groups in perfragilin B causes the isoquinoline ring system to exhibit significant deviations from planarity [r.m.s. deviation 0.067 (1) Å].

Comment

Perfragilin A and B [(I) and (II) respectively; see scheme below] are two new metabolites from a bryozoan, *Membranipora perfragilis* (Schmitz, DeGuzman, Choi, Hossain, Rizvi & van der Helm, 1990). Both compounds show cytotoxic activity on P388 murine leukemia cells with compound (II) nearly 20 times more active than (I) (Choi, Schmitz & van Altena, 1992). The perfragilins are derivatives of basic isoquinolinetrione and bear a close resemblance to mimosamycin which is produced by *Streptomyces lavendulae* (Fukumi, Kurihara, Hata, Tamura, Mishima, Kubo & Arai, 1977; Hata, Fukumi, Sato, Aiba & Tamura, 1978). The novel feature of the perfragilins is the presence of a thiomethyl group in place of the methoxy and methyl groups found in mimosamycin. It has recently been observed in some naturally occurring alkaloids (varamines and diplamine) that the cytotoxicity of compounds with a similar ring structure is increased by an order of magnitude by the introduction of a thiomethyl group (Charyulu, McKee & Ireland, 1989). An additional thiomethyl group in perfragilin B enhances its cytotoxicity, indicating that the thiomethyl group may play an important role in bioactivity. The structure determination of the two compounds was undertaken to establish the chemical structures of the two perfragilins and to obtain a better understanding of the effect of structural change on biological activity.

