are two of these per unit cell, each residing on an inversion center. Each ring N atom is protonated, as is clear not only from the stoichiometry but from actual observation of these H atoms in a difference map. The pyridinium rings are essentially coplanar with the attached carboxyl groups. The axial chloride ligands are only loosely bound at a distance of 2·835 (1) Å. This is quite typical for axial Mo—Cl bonds in Mo$_2$(O$_2$CR)$_4$Cl$_2$ species, where five previously observed values are in the range 2·829 (2) to 2·907 (1) Å, with a mean of 2·869 Å (Bino & Cotton, 1980). The Mo—Mo distance of 2·122 (1) Å is comparable to other such bond lengths in similar compounds.

All H atoms were found and refined, and their positions are listed in the deposited material.

In the pyridinium rings the ten N—H and C—H distances range from 0·84 (3) to 0·99 (3) Å with an average value of 0·91 Å and an average e.s.d. of 0·04 Å. The six O—H distances in the water molecules ranged from 0·93 (3) to 1·11 (3) Å with an average value of 1·00 Å and an average e.s.d. of 0·03 Å.

There is an extensive set of hydrogen bonds throughout the crystal. The water molecules H(15)—O(6)—H(16) and H(17)—O(7)—H(18) are linked into an infinite chain ···H(15)—O(6)···H(18)—O(7)···, with alternating O to O distances of 2·83 and 2·84 Å. The free chloride ion,

Cl(2), interacts with N(1), O(5) and O(7) at distances of 3·01, 3·10 and 3·32 Å, respectively. The corresponding angles about the H atoms [Cl(2)···H(1)—N(1), 146 (3), Cl(2)···H(13)—O(5), 173·1 (2) and Cl(2)···H(17)—O(7), 156·2 (2)°] along with the contact distances, indicate that these are hydrogen-bond interactions. The hydrogen bonds mediate the packing in this structure, in which there are no van der Waals contacts between pyridinyl moieties of adjacent molecules.

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Structures of Tetraethylammonium Tetrachloroferrate(III) and the Mixed Halide Iron(III) Complex, [NEt$_4$][FeBrCl$_3$]

BY DAVID J. EVANS, ADRIAN HILLS, DAVID L. HUGHES AND G. JEFFERY LEIGH

AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, England

Abstract. Tetraethylammonium tetrachloroferrate-(III), [N(C$_2$H$_5$)$_4$][FeCl$_4$], M_r = 327·91, hexagonal, $P6_3mc$, a = 8·212 (1), c = 13·201 (1) Å, V = 770·9 Å^3, Z = 2, $F(000)$ = 338, D_x = 1·413 g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, μ = 16·5 cm^{-1}, T = 293 K, R = 0·055 for all 293 reflections. Tetraethylammonium bromotrichloroferrate(III), [N(C$_2$H$_5$)$_4$][FeBrCl$_3$], M_r = 372·36, hexagonal, $P6_3mc$, a = 8·230 (1), c = 13·242 (1) Å, V = 776·7 Å^3, Z = 2, D_x = 1·592 g cm^{-3}, $F(000)$ = 374, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, μ = 40·1 cm^{-1}, T = 293 K, R = 0·055 for all 295 reflections. The crystals are isostructural; in both cases, the cations are disordered about a $3m$ symmetry site. The [FeCl$_4$]$^-$ ion is well resolved with $3m$ (and almost perfect tetrahedral) symmetry and mean Fe—Cl 2·185 (1) Å. The [FeBrCl$_3$]$^-$ ion is disordered with Br replacing Cl in either of its two sites.

Introduction. The title compound [NEt$_4$][FeBrCl$_3$] was initially obtained as a by-product of reactions to prepare novel Fe$_4$S$_4$ metal clusters by 'spontaneous self-assembly' reactions. Below a direct procedure is

reported to this mixed halide iron(III) complex. [NEt$_4$][FeCl$_4$] was prepared and the crystal structure determined as an aid in the refinement of the crystal structure of [NEt$_4$][FeBrCl$_3$].

Experimental.
[NEt$_4$][FeCl$_4$]

Tetraethylammonium tetrachloroferrate(III) was prepared by mixing solutions of iron(III) chloride (3·14 g, 20 mmol) in dry methanol (35 cm^3) and tetraethylammonium chloride (2·44 g, 15 mmol) in dry methanol (25 cm^3). The flocculent yellow precipitate was recrystallized from methanol at 298 K to give yellow rectangular prisms.

[NEt$_4$][FeBrCl$_3$]

Prepared by mixing solutions of iron(III) chloride (6·30 g, 39 mmol) in dry methanol (20 cm^3) and tetraethylammonium bromide (5·70 g, 27 mmol) in dry methanol (25 cm^3). Recrystallization from methanol at 253 K gave orange needles.

X-ray analysis of [NEt$_4$][FeBrCl$_3$]

A crystal, ca 0·14 × 0·14 × 0·33 mm, was examined photographically and transferred to an Enraf–Nonius CAD-4 diffractometer (with monochromated Mo radiation) for determination of accurate cell dimensions (from 25 reflections with θ ca 10·5°, each centred in four orientations) and measurement (by an ω/θ scan method) of 328 diffraction intensities (to θ_{max} 25°; h, k 0–9; l 0–15). During processing, corrections were applied for Lorentz–polarization effects, absorption (by semi-empirical ψ-scan methods; $t_{max}, t_{min} = 1·00, 0·98$) and for negative intensities (by Bayesian statistical methods); no deterioration correction was necessary (two reflections monitored every 10 000 s of exposure time showed no change in intensity throughout the data collection).

Intensities for 295 unique reflections, 218 of which had $I > 2\sigma(I)$, were input to the SHELX program system (Sheldrick, 1976). E statistics suggested a non-centrosymmetric lattice, and automatic Patterson routines in SHELXS (Sheldrick, 1985) confirmed a structure analogous to that of [NEt$_4$][InCl$_4$] in the space group $P6_3mc$ (Trotter, Einstein & Tuck, 1969). Refinement (on F) of the Fe, Cl, N and outer, C_β, carbon atoms, with anisotropic thermal parameters, by full-matrix least-squares methods reduced R to ca 0·125 (for all the data) but identification of the Br atom site(s) and the arrangement of the C_α atoms was not clear.

After refinement of the [FeCl$_4$]$^-$ crystals (see below), coordinates for the cation in that structure were taken and included in the [NEt$_4$][FeBrCl$_3$] refinement. Br-atom sites were estimated and, initially, restrained to be ca 0·35 Å from the Cl positions. Reversing the polarity of the structure

Table 1. *Final atomic parameters* ($\times 10^4$) *and isotropic or equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *with e.s.d.'s in parentheses for* (a) [NEt$_4$][FeBrCl$_3$], (b) [NEt$_4$][FeCl$_4$]

	x	y	z	U_{iso}/U_{eq}	S.o.f.*
(a) [NEt$_4$][FeBrCl$_3$]					
Fe(1)	0	0	5000	69 (1)†	
Cl(2)	0	0	3400 (28)	101 (11)†	0·8562
Br(2)	0	0	3182 (87)	75 (13)†	0·1438
Cl(3)	−1432 (7)	1432 (7)	5557 (12)	97 (3)†	0·9506
Br(3)	−1707 (37)	1707 (37)	5520 (62)	62 (14)†	0·0494
N(4)	6667	3333	2437 (12)	56 (4)†	
C(41)	6738 (41)	1505 (38)	2428 (28)	40 (6)	0·1667
C(41x)	6109 (28)	3891 (28)	3438 (25)	98 (11)	0·3333
C(41y)	8745 (115)	4372 (58)	2232 (51)	176 (25)	0·3333
C(42)	5001 (20)	2 (40)	3092 (22)	179 (11)†	
C(43)	5429 (52)	2715 (26)	1591 (29)	100 (10)	0·3333
C(44)	6667	3333	520 (19)	240 (24)†	
(b) [NEt$_4$][FeCl$_4$]					
Fe(1)	0	0	5000	69·0 (6)†	
Cl(2)	0	0	3345 (3)	96 (2)†	
Cl(3)	−1450 (2)	1450 (2)	5545 (4)	105 (1)†	
N(4)	6667	3333	2427 (10)	53 (3)†	
C(41)	6690 (32)	1488 (30)	2466 (22)	40 (4)	0·1667
C(41x)	6101 (26)	3899 (26)	3406 (19)	88 (8)	0·3333
C(41y)	8656 (100)	4328 (50)	2130 (43)	169 (21)	0·3333
C(42)	4967 (17)	−66 (34)	3049 (22)	182 (11)†	
C(43)	5463 (42)	2732 (21)	1535 (20)	81 (7)	0·3333
C(44)	6667	3333	498 (13)	211 (19)†	

* S.o.f. = site occupancy factor, if different from 1·0.
† Equivalent isotropic thermal parameter, defined as: U_{eq} = one third the trace of the orthogonalized U_{ij} tensor.

decreased the R factor slightly. Finally, the part-Br atoms were released from geometrical restraints and allowed anisotropic thermal parameters, giving refinement for 48 parameters to $R = 0·055$ and $wR = 0·045$ for all 295 reflections, weighted $w = \sigma_F^{-2}$; in the final cycle, max. shift/e.s.d. = 0·046. The major peaks in a final difference map, at ca 0·5 e Å^{-3}, were in the cation region.

In the refinement, the proportions of Br to Cl were allowed to vary and the thermal parameters of these atoms were not related. This procedure was not totally satisfactory and we appear to have, overall, rather less than one Br atom per anion. We believe this results from inadequacies in the diffraction data and, hence, in the refinement process, rather than from any variation in stoichiometry from the [FeBrCl$_3$]$^-$ formula.

Atomic coordinates are listed in Table 1(a).*

X-ray analysis of [NEt$_4$][FeCl$_4$]

Crystals are clear, yellow rectangular prisms. One, ca 0·14 × 0·24 × 0·64 mm, was examined in a pro-

Table 2. *Molecular dimensions* (Å,°) *with e.s.d.'s in parentheses for* (a) [NEt₄][FeBrCl₃], (b) [NEt₄][FeCl₄]

(a) [NEt₄][FeBrCl₃]
(i) In the anion

Fe(1)—Cl(2)	2·12 (4)		Fe(1)—Cl(3)	2·170 (11)
Fe(1)—Br(2)	2·41 (12)		Fe(1)—Br(3)	2·53 (6)
Cl(2)—Fe(1)—Cl(3)	109·9 (4)		Cl(3)—Fe(1)—Cl(3')	109·1 (3)
Br(2)—Fe(1)—Cl(3)	109·9 (4)		Cl(3)—Fe(1)—Br(3')	111·1 (11)
Cl(2)—Fe(1)—Br(3)	105·8 (18)			

(ii) In the cation

N(4)—C(41)	1·53 (3)		C(41)—C(42)	1·61 (4)
N(4)—C(41x)	1·55 (4)		C(41x)—C(42″)	1·64 (3)
N(4)—C(41y)	1·51 (8)		C(41y)—C42‴)	1·45 (8)
N(4)—C(43)	1·43 (4)		C(43)—C(44)	1·67 (4)
C(41)—N(4)—C(41x)	117·4 (20)		C(41y)—N(4)—C(43)	117·8 (34)
C(41)—N(4)—C(41y)	88·1 (11)		N(4)—C(41)—C(42)	107·2 (21)
C(41x)—N(4)—C(41y)	114·0 (24)		N(4)—C(41x)—C(42″)	104·8 (21)
C(41)—N(4)—C(43)	90·8 (14)		N(4)—C(41y)—C(42‴)	117·7 (48)
C(41x)—N(4)—C(43)	121·0 (15)		N(4)—C(43)—C(44)	109·9 (24)

(b) [NEt₄][FeCl₄]
(i) In the anion

Fe(1)—Cl(2)	2·184 (4)		Fe(1)—Cl(3)	2·185 (3)
Cl(2)—Fe(1)—Cl(3)	109·2 (1)		Cl(3)—Fe(1)—Cl(3')	109·7 (1)

(ii) In the cation

N(4)—C(41)	1·53 (2)		C(41)—C(42)	1·55 (3)
N(4)—C(41x)	1·52 (3)		C(41x)—C(42″)	1·68 (3)
N(4)—C(41y)	1·47 (7)		C(41y)—C(42‴)	1·57 (7)
N(4)—C(43)	1·46 (3)		C(43)—C(44)	1·61 (3)
C(41)—N(4)—C(41x)	115·6 (16)		C(41y)—N(4)—C(43)	110·5 (29)
C(41)—N(4)—C(41y)	89·9 (9)		N(4)—C(41)—C(42)	112·0 (17)
C(41x)—N(4)—C(41y)	118·8 (20)		N(4)—C(41x)—C(42″)	105·6 (17)
C(41)—N(4)—C(43)	91·9 (11)		N(4)—C(41y)—C(42‴)	114·1 (38)
C(41x)—N(4)—C(43)	122·1 (13)		N(4)—C(43)—C(44)	112·0 (19)

Atoms with primed numbers occupy symmetry-related sites.

cedure which followed closely that described above; the only differing details concern the absorption correction, where t_{max}, $t_{min} = 1·00, 0·87$. Intensities for 293 unique reflections, 258 of which have $I > 2\sigma(I)$, were input to the *SHELX* program system. Preliminary parameters for the Fe, Cl, N and C_β atoms were taken from the [FeBrCl₃]⁻ analysis and refined by full-matrix least-squares methods. Difference Fourier maps showed peaks corresponding to a disordered array of ethyl groups in the cation. Refinement of 37 parameters was continued to convergence at $R = 0·055$ and $wR = 0·048$ for all data, weighted $w = \sigma_F^{-2}$, in the final cycle, max. shift/e.s.d. $= 0·002$. A final difference map showed the strongest peaks (*ca* 0·3 e Å⁻³) around the C_β atoms of the cation.

A trial refinement of the structure in the opposite polarity showed no significant difference from the structure having the coordinates listed in Table 1(*b*).

For both analyses, scattering factor curves for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Computer programs, noted above and listed by Anderson, Richards & Hughes (1986), were run on a DEC-MicroVAX II machine.

Discussion. Crystals of the [FeCl₄]⁻ and [FeBrCl₃]⁻ salts, and of the previously reported [NEt₄][InCl₄] (Trotter, Einstein & Tuck, 1969), are isostructural, and all show features of disorder in the cation. We have been able to resolve some details of the [NEt₄]⁺ ions in our crystals but the dimensions in the refined structures are not altogether acceptable (Tables 2a,b). The nitrogen atom N(4) is placed confidently on the threefold symmetry axis, and the four C_β atoms are on, or close to, sites of 3m or m symmetry in a trigonal pyramidal (almost tetrahedral) pattern about N(4) (see Fig. 1). The C_α atoms show sixfold disorder within this arrangement, with C(41) in a general position, and C(41x) and C(41y) lying on (or close to) mirror planes. The apparently poor molecular dimensions result, we believe, from the deviations of atoms in any one cation from the ideal symmetry sites.

The anion [FeCl₄]⁻ has almost perfect tetrahedral symmetry; Fe(1) and one Cl atom, Cl(2), lie on 3m positions, with Cl(3) and its symmetry relations on the mirror planes. The Fe—Cl distances are almost identical to those found in [AsPh₄][FeCl₄], 2·182 (1) Å (Cotton & Murillo, 1975), but the symmetry restraints in our crystal do not allow the same type of tetragonal distortion found in the arsonium salt; in fact, the angles about Fe(1) in our [FeCl₄]⁻ salt are very close to the regular tetrahedral angle.

In the [FeBrCl₃]⁻ ions, the Br atom replaces a Cl atom in either site, with distortions from 3m symmetry when Br(3) is present. The low precision of the dimensions in this ion reflect the disorder therein.

All interionic contacts, in both crystals, are between the halogen atoms and the methylene (C_α) groups, with several Cl···C_α distances of 3·61 (2)–3·70 (5) Å in the [FeCl₄]⁻ salt and 3·59 (3)–3·75 (6) Å
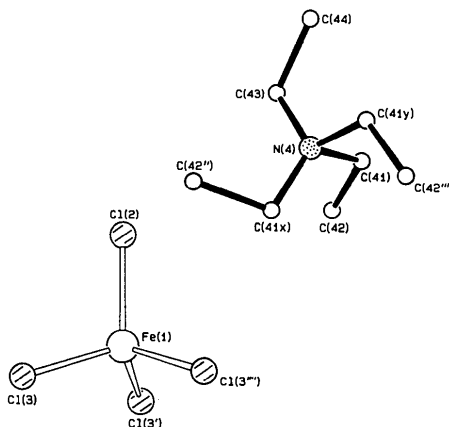

Fig. 1. View of the ions in [NEt₄][FeCl₄]. One of the six disordered orientations of the cations is shown. Crystals of [NEt₄][FeBrCl₃] are isostructural, with similar disorder in the cation and additional disorder in the anion.

in the [FeBrCl₃]⁻ sample. In the latter crystal, where we have noted disorder in both cation and anion, Br···C_α distances calculated at 3·43 (7) and 3·61 (4)– 3·69 (8) Å are probably not found between any pair of ions.

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Structure of [(*S*)-2,5-Di(salicylideneamino)-1-pentanoato(3 −)](pyridine)cobalt(III), [Co(sal₂pen)py]*

BY J. ONDRÁČEK

Department of Solid State Chemistry, Institute of Chemical Technology, 166 28 Praha 6, Czechoslovakia

F. JURSÍK

Department of Inorganic Chemistry, Institute of Chemical Technology, 166 28 Praha 6, Czechoslovakia

AND J. MAIXNER AND B. KRATOCHVÍL

Department of Solid State Chemistry, Institute of Chemical Technology, 166 28 Praha 6, Czechoslovakia

Abstract. $C_{24}H_{22}CoN_3O_4$, $M_r = 475\cdot4$, monoclinic, $P2_1$, $a = 8\cdot989$ (1), $b = 11\cdot187$ (1), $c = 11\cdot067$ (2) Å, $\beta = 104\cdot43$ (2)°, $V = 1077\cdot8$ (3) Å³, $Z = 2$, $D_m = 1\cdot455$, $D_x = 1\cdot465$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu(\text{Mo } K\alpha) = 0\cdot83$ mm⁻¹, $F(000) = 492$, $T = 296$ K, $R = 0\cdot035$ for 3230 unique observed reflections. The complex exhibits distorted octahedral geometry with the sal₂pen [(*S*)-2,5-di(salicylideneamino)-1-pentanoate] ligand coordinated stereospecifically through nitrogens and phenolic and carboxylic oxygens in meridional fashion. The six-membered rings adopt envelope conformations. The degree of the chelate-ring flattening depends on the Co—donor atom distance. Different Co—O(phenoxide) and Co—N(=C) bonds are observed.

Introduction. Much attention has been devoted to Schiff-base metal complexes of the salicylaldimine type due to their ability to mimic transformations catalyzed by enzymes requiring pyridoxal phosphate as cofactor (Jursík & Hájek, 1974), and to serve as

possible models of iron–tyrosinate and/or iron–imidazole proteins (Davis, Kung & Averill, 1986). As a first step in the study of metal complexes of these ligands as possible active site models a detailed knowledge of their principal stereochemistry is required. To confirm the mode of ligand coordination and to establish a standard for correlation of physicochemical properties with structure for this type of complex, we describe in this paper the crystal and molecular structure of [Co(sal₂pen)py].

Experimental. The title complex was prepared by the addition of solid *trans*-[CoCl₂(py)₄]Cl (0·01 mol) to a methanolic solution containing (*S*)-ornithine free base (0·01 mol) and salicylaldehyde (0·02 mol). Crystals that separated from this solution overnight were filtered off and recrystallization from pyridine yielded brown plate-like crystals. Calculated for $C_{24}H_{22}CoN_3O_4$: C 60·63, H 4·66, N 8·84%, and found: C 60·57, H 4·74, N 8·78%. The density determination was carried out by flotation in iodomethane/toluene mixture at 298 K.

Crystal size 0·40 × 0·33 × 0·07 mm, Enraf–Nonius CAD-4 SDP73 system, lattice parameters refined from setting angles (19 < θ < 20°) of 25 centered

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* Part IX in the series: Transition Metal Complexes of Ligands Containing the Azomethine Group. Part VIII: Jursík, Kvasnicq & Hájek (1980).