tuation ($\sigma_{Ru-Cl}=0{\cdot}007$ Å). We believe that the greater bond length corresponding to the equatorially substituted chlorine atom is to be attributed to a repulsive effect on the Ru–Cl bonding electrons induced by the allylic π-electrons donated to the metal (see Fig. 3). Owing to the geometry of the coordination, the above effect is analogous to the well-known *trans* effect. Contrary to the case of most dimeric complexes containing chlorine bridges, the Ru_2Cl_2 planar four-membered ring deviates appreciably from the perfect square conformation: in addition to the above discussed difference in the Ru–Cl bond lengths, the Cl–Ru–Cl and Ru–Cl–Ru angles are quite different from 90° (75·2° and 104·8° respectively, see Fig. 1).

We express our gratitude to Drs Porri and Vitulli for providing us with the crystalline samples, and for very useful discussions.

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The Crystal Structure of 4-Ethylpyridinium Tetrabromoferrate(III)[*]

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Single-crystals of 4-ethylpyridinium tetrabromoferrate(III) have been prepared and their crystal structure has been determined by three-dimensional X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a=7{\cdot}7068$ (8), $b=14{\cdot}1673$ (11), $c=13{\cdot}0414$ (16) Å, $\beta=84{\cdot}19$ (1)°, and $Z=4$. Intensity data were measured using a θ–2θ step scan technique on an automated diffractometer with Mo $K\alpha$ radiation. The structure was solved by superposition and Fourier methods and refined by full-matrix least-squares techniques to a final residual R of 0·061 for the 762 observed reflections used in the analysis. Ring atoms of the cation were refined as a rigid group. The $FeBr_4^-$ tetrahedra are nearly aligned with their threefold axes almost coincident in the **c** direction. Average Fe–Br distance is 2·326 Å (this average becomes 2·347 Å when the interatomic distances are corrected for thermal motion assuming a riding model). The structure is in part stabilized by the presence of a weak N–H---Br hydrogen bond.

Introduction

The crystal-structure study of 4-ethylpyridinium tetrabromoferrate(III) was undertaken after the compound accidentally appeared as a byproduct during a series of investigations of bromo-coordinated antimony compounds in this laboratory. The true composition was determined from the crystal-structure analysis and also by an electron-microprobe analysis of the crystal used in the data collection. We felt it would be of interest to complete the crystal-structure analysis of the tetrabromoferrate(III) compound because of the general instability of iron(III)bromides (Sidgwick, 1950) and the lack of crystal-structure data regarding the $FeBr_4^-$ group.

Experimental

Crystal data

4-Ethylpyridinium tetrabromoferrate(III),
$C_7H_9NHFeBr_4$,
$M=483{\cdot}65$, monoclinic $P2_1/c$, $F(000)=900e$, $Z=4$,
$a=7{\cdot}7068$ (8), $b=14{\cdot}1673$ (11), $c=13{\cdot}0414$ (16) Å,
$\beta=84{\cdot}19(1)$°,
$V=1416{\cdot}6$ Å^3, $D_c=2{\cdot}27$ g.cm^{-3},
Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å), $\mu=135{\cdot}8$ cm^{-1}.

Single crystals of $C_7H_9NHFeBr_4$ were obtained accidentally from contamination introduced into a vessel where the corresponding antimony bromide salt was being prepared. Of the two crystalline forms present, crystals of what later was determined to be the tetra-

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bromoferrate(III) salt were selected because their crystal habit was more suitable for X-ray analysis; the other crystals had one very short dimension. The true composition was later determined from crystal-structure analysis and electron-microprobe analysis.

The compound has subsequently been prepared by adding 4-ethylpyridine to a solution containing iron and Br_2 in concentrated hydrobromic acid. In this preparation a deep red-black crystalline solid forms very slowly upon cooling. (An alternate preparation of similar tetrahaloferrate ions has been reported by Clausen & Good, 1969.) Precession photographs of these crystals are identical with those obtained from the crystal used in data collection. These photographs exhibited $2/m$ Laue symmetry with the following systematic absences: $0k0$ when $k=2n+1$ and $h0l$ when $l=2n+1$. These extinctions uniquely specify the monoclinic space group $P2_1/c$. The unit-cell dimensions and their standard deviations were obtained by a least-squares fit to 13 independent reflection angles whose centers were obtained by carefully aligning the crystal on a General Electric single-crystal orienter using a 1° take-off angle and Cr $K\alpha_1$ radiation ($\lambda=2{\cdot}28962$ Å).

The crystal used for data collection was approximately $0{\cdot}14\times0{\cdot}15\times0{\cdot}35$ mm. It was mounted in a 0·2 mm thin-walled, Lindemann glass capillary tube with the c axis (0·35 mm) nearly parallel to the φ axis. Data were taken at room temperature ($T\approx24°$) utilizing a fully automated Hilger–Watts four-circle diffractometer equipped with scintillation counter. Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) radiation was used with balanced (Zr–Y) filters to obtain intensity and individual background readings. The 2θ–θ step scan technique with a 4·5° take-off angle was used to record 1751 reflections within a 2θ sphere of 50° ($\sin\theta/\lambda=0{\cdot}595$ Å^{-1}). A variable scan range was employed of 50 steps plus 2 per deg θ at a counting rate of 0·2048 sec per step of 0·01 deg in θ. As a general check on electronic and crystal stability, the intensities of three standard reflections were remeasured periodically during the data collection. Comparison of these values indicated that no decomposition had occurred.

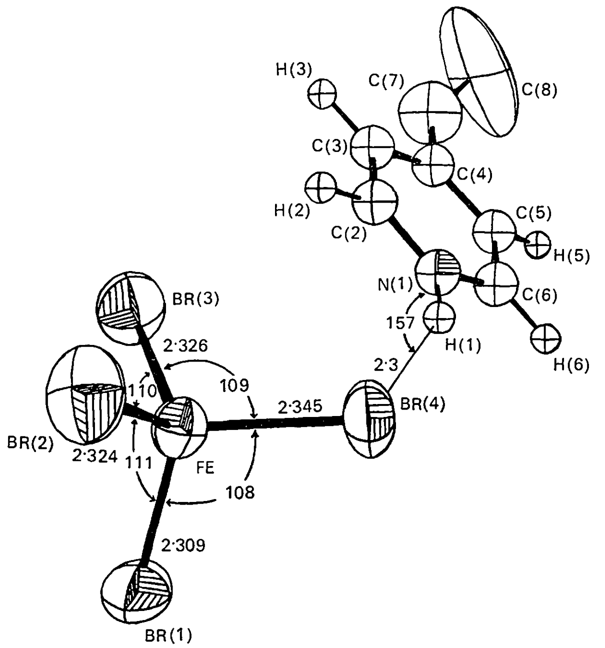

Fig. 1. Formula unit of 4-ethylpyridinium tetrabromoferrate(III) with important bond distances (Å) and angles (°) and showing presence of N–H---Br hydrogen bond.

Intensity data were corrected for Lorentz–polarization effects and for effects due to absorption ($\mu=135{\cdot}8$ cm^{-1}). The absorption correction was made using program *ABCOR* (Busing & Levy, 1957); the maximum and minimum transmission factors were 0·215 and 0·196, respectively. Estimated error in each intensity measurement was calculated by

$$[\sigma(I)]^2=[C_T+C_B+(0{\cdot}05C_T)^2+(0{\cdot}10C_B)^2+(0{\cdot}05C_R)^2]/A^2$$

where C_T, C_B, C_R and A are the total count, background count, net count and the transmission factor, respectively. The estimated standard deviation of each structure factor was calculated from the estimated errors in the intensity using the finite-differences method of Williams & Rundle (1964). Reciprocals of the structure factor variances were used as the weights during the refinement. Based on the measurement of symmetry extinct reflections, it was decided that only those reflections for which $I>3\sigma(I)$ would be considered observed. The results reported below are based on the 762 remaining observed reflections.

Solution and refinement

The observed Patterson synthesis was difficult to interpret because of preconceived notions regarding the distances and geometry expected for antimony-bromide polyhedra. A series of single superpositions was then carried out using general peaks on a sharpened Patterson map. Comparison of the resulting maps revealed an MX_4 heavy-atom group of tetrahedral geometry. These coordinates were input as an $SbBr_4$ group with fixed thermal parameters and were refined by a full-matrix least-squares procedure* minimizing the function $\sum w(|F_o|-|F_c|)^2$. Examination of the resulting electron-density map revealed all nonhydrogen atom positions. Isotropic refinement resulted in a conventional R value, $R=[\sum(|F_o|-|F_c|)]/\sum|F_o|$, of 0·185 and a weighted R value, $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{\frac{1}{2}}$, of 0·223.

The multiplier of the metal atom was then allowed to vary while the scale and its thermal parameters remained fixed. The multiplier varied from 1·00 to 0·53, lowering the discrepancy factor to $R=0{\cdot}156$. This im-

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* In additional to local programs written at this laboratory, the authors wish to acknowledge the use of *ACBOR* (Busing & Levy), *ORTEP* (C. K. Johnson), *ORFFE* and a local modification *ORFLS* (Busing, Martin & Levy) and *LCR*2 (D. E. Williams).

Table 1. *Final positional and thermal parameters for* $C_7H_9NHFeBr_4$*

Standard errors of the coordinates and the β_{ij} and their standard errors are $\times 10^4$. The β_{ij} are defined by:

$$T=\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0·3045 (4)	0·2603 (2)	0·0646 (3)	181 (7)	61 (2)	59 (3)	2 (3)	−20 (3)	3 (2)
Br(1)	0·3562 (4)	0·1058 (2)	0·0138 (2)	363 (8)	60 (2)	92 (3)	21 (3)	−13 (4)	−3 (2)
Br(2)	0·0310 (4)	0·3096 (3)	0·0259 (2)	222 (7)	123 (3)	97 (3)	56 (3)	−33 (3)	−5 (2)
Br(3)	0·5212 (4)	0·3567 (3)	−0·0163 (3)	317 (8)	108 (3)	92 (3)	−66 (4)	−6 (4)	13 (2)
Br(4)	0·3148 (4)	0·2673 (2)	0·2435 (2)	304 (7)	103 (2)	52 (2)	−24 (3)	−18 (3)	−3 (2)
C(8)	1·1980 (60)	0·6012 (49)	0·3054 (37)	568 (148)	443 (89)	200 (57)	−217 (97)	−132 (70)	−160 (60)

plied that the central metal atom was smaller than an antimony, atomic number ≈ 27, in agreement with the shorter M–Br distances found. An electron-microprobe analysis of the crystal used for data collection confirmed the absence of antimony and indicated the presence of iron and bromine. Preliminary treatment of the data was then repeated. (The results described earlier were based on the iron compound and included the revised absorption coefficient.) Subsequent refinement based on $FeBr_4$ proceeded smoothly and with anisotropic thermal parameters for all nonhydrogen atoms converged to a discrepancy factor of $R=0{\cdot}056$ and $R_w=0{\cdot}089$.

Unusually large thermal ellipsoids were obtained for the ethyl carbon atoms, and a least-squares plane analysis of the pyridinium-ring atoms revealed deviations as large as 0·05 Å; therefore, it was decide to use rigid-body refinement for the ring and adjacent atoms. The C–N bond length was taken as 1·340 Å and the four C–C lenghts as 1·394 Å each (Bak, Hansen-Nygaard, & Rastrup-Andersen, 1958). This decreased the number of variables from 118 to 62; refinement converged to a discrepancy factor of $R=0{\cdot}061$ and a weighted discrepancy factor of $R_w=0{\cdot}096$. A final electron-density difference map showed no peak heights greater than 0·4 e.Å^{-3}.

The relativistic Hartree–Fock X-ray scattering factors for neutral atoms of Doyle & Turner (1968) were used, with those of iron and bromine being modified for the real and imaginary parts of anomalous dispersion (Templeton, 1962). The scattering factor used for hydrogen was the contracted form of Stewart, Davidson & Simpson (1965). Based on the agreement of the large structure factors, no extinction correction was necessary. The final positional and thermal parameters and their standard errors as derived from the inverse matrix of the final least-squares cycle are given in Table 1. Positional coordinates of the group atoms are listed in Table 2. Final values of the observed and calculated structure factors (× 10) are listed in Table 3.

Table 2. *Group parameters for* $C_7H_9NHFeBr_4$*

$x_o=0{\cdot}6708\ (21)$ $\varrho=\ 8{\cdot}91\ (35)$
$y_o=0{\cdot}3869\ (13)$ $\theta=-45{\cdot}63\ (83)$
$z_o=0{\cdot}2868\ (15)$ $\varphi=\ 39{\cdot}77\ (86)$

Group $B=3{\cdot}96\ (35)$ Å^2

	x	y	z
N(1)	0·6708	0·3869	0·2868
C(2)	0·6928	0·4563	0·2168
C(3)	0·8419	0·5123	0·2023
C(4)	0·9764	0·4957	0·2638
C(5)	0·9557	0·4239	0·3369
C(6)	0·8013	0·3719	0·3453
C(7)	1·1442	0·5555	0·2512
H(1)	0·5564	0·3462	0·2953
H(2)	0·5897	0·4700	0·1685
H(3)	0·8530	0·5674	0·1447
H(5)	1·0569	0·4088	0·3861
H(6)	0·7872	0·3164	0·4023

* The group was defined in the xy plane of the orthogonal coordinate system with the twofold axis along x; x_o, y_o and z_o refer to the group origin and ϱ, θ and φ are the rotation angles in degrees (Scheringer, 1963). In addition to the group thermal parameter, the fixed individual thermal parameters assigned group atoms were 3·5, 8·5 and 6·0 Å^2 for the ring atoms, C(7) and hydrogen atoms, respectively.

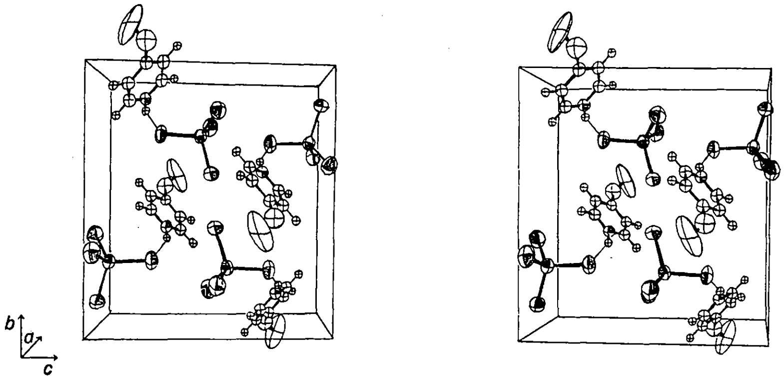

Fig. 2. Stereogram of unit cell showing packing of 4-ethylpyridinium tetrabromoferrate(III) units.

Description of the structure

The tetrabromoferrate(III) group describes a slightly distorted tetrahedron with bond distances ranging from 2·309 to 2·345 Å and bond angles of 107·7 to 110·9°, the averages being 2·326 Å and 109·5°. This average Fe–Br distance becomes 2·347 Å (range 2·328 to 2·362 Å) when interatomic distances are corrected for thermal

Table 3. *Observed and calculated structure factors* (× 10)

H	L	FO	FC
K = 0			
1	0	1057	-1041
3	0	2199	2140
4	0	600	598
5	0	749	-712
6	0	899	927
-5	2	276	202
-4	2	1011	1127
-3	2	242	192
-2	2	1634	1510
-1	2	193	175
0	2	1618	1758
1	2	1991	-1857
2	2	2809	2724
3	2	191	219
6	2	288	336
7	2	386	-393
-6	4	421	434
-5	4	280	-217
-4	4	672	695
-3	4	1253	1203
0	4	3594	4040
1	4	2249	-2193
2	4	1006	998
3	4	1212	1185
4	4	270	-248
5	4	573	-516
6	4	726	705
7	4	379	-402
-5	6	550	535
-4	6	602	664
-3	6	392	-340
-2	6	702	775
-1	6	762	773
0	6	454	396
1	6	1040	-968
2	6	2279	2297
3	6	1031	-1038
4	6	584	-582
5	6	357	403
-3	8	547	609
-2	8	283	301
-1	8	207	-293
0	8	954	1044
1	8	820	-759
2	8	259	263
3	8	266	-233
5	8	339	-311
0	10	289	-285
1	10	318	-339
2	10	664	652
3	10	852	-897
5	10	225	135
-1	12	395	-449
0	12	446	446
2	12	274	-352
K = 1			
1	0	2235	-2243
2	0	1471	1367
3	0	216	206
4	0	1904	-1981
5	0	300	268
7	0	348	-417
9	0	282	-236
-4	1	671	-755
-3	1	843	829
-2	1	1213	-1205
-1	1	186	198
0	1	145	-103
1	1	399	-448
2	1	1051	-1019
3	1	729	697
4	1	995	-914
5	1	262	299
-6	2	329	378
-4	2	473	477
-3	2	489	-476
-2	2	730	706
-1	2	434	329
0	2	867	-922
1	2	639	-575
3	2	1306	-1275
4	2	683	-680
6	2	683	-713
-4	3	826	-823
-3	3	468	515
-2	3	1140	-1092
-1	3	356	-319
0	3	463	-454
1	3	489	-443
2	3	980	-969
3	3	801	744
4	3	737	-763
5	3	372	293
-4	4	853	884
-3	4	954	-990
-2	4	334	-319
-1	4	801	768
0	4	1158	-1190
1	4	2001	-1868
2	4	909	879
3	4	1195	-1193
4	4	1247	-1269
5	4	284	274
6	4	476	-498
7	4	304	-416
-4	5	441	-475
-3	5	587	579
-2	5	851	-892
2	5	393	-320
3	5	712	701
4	5	483	-530
5	5	370	410
-6	6	298	325
-4	6	313	-317
-3	6	534	-494
-2	6	911	975
-1	6	1361	-1389
0	6	1051	-1075
1	6	363	313
2	6	452	-418
3	6	1725	-1692
4	6	295	270
6	6	762	-812
-4	7	339	-260
-3	7	259	285
-2	7	658	-680
-1	7	223	221
0	7	189	124
1	7	255	-283
2	7	266	-238
3	7	525	466
4	7	436	-435
5	7	299	340
-5	8	385	-416
-4	8	331	293
-3	8	364	-340
-2	8	411	-428
-1	8	370	-307
1	8	996	-998
3	8	590	-602
4	8	308	-262
-2	10	255	243
-1	10	835	-873
2	10	420	-491
3	10	725	-659
4	10	480	443
0	12	337	259
1	12	739	-750
K = 2			
0	0	1937	-2143
1	0	463	422
2	0	267	304
3	0	1479	-1457
4	0	593	-623
5	0	539	560
6	0	369	-394
7	0	264	-254
-8	1	314	-281
-5	1	434	-456
-4	1	316	-320
-3	1	819	809
-2	1	1745	-1667
-1	1	629	641
0	1	558	620
1	1	455	-463
2	1	1332	1330
3	1	247	237
4	1	543	520
5	1	289	325
6	1	251	287
-7	2	357	-306
-5	2	267	-276
-4	2	979	-983
-3	2	348	295
-2	2	794	-901
-1	2	2081	-2043
0	2	926	-964
1	2	377	-345
2	2	1412	-1424
3	2	173	-136
4	2	260	-234
5	2	275	-239
-4	3	243	-215
-3	3	277	212
-2	3	939	-939
-1	3	2118	2051
0	3	373	-375
1	3	130	-67
2	3	1351	1291
3	3	262	-263
4	3	406	474
5	3	608	615
-4	4	771	-741
-3	4	557	-587
-1	4	418	-399
0	4	1157	-1211
1	4	391	415
2	4	344	-339
3	4	722	-744
4	4	200	175
5	4	393	409
6	4	331	-338
-6	5	215	-154
-3	5	721	666
-2	5	1024	-983
-1	5	1183	1116
0	5	196	-203
1	5	331	321
2	5	776	817
3	5	369	363
4	5	331	357
5	5	305	290
-5	6	517	-573
-4	6	486	-536
-3	6	768	721
-2	6	889	-902
-1	6	1297	-1299
0	6	907	942
2	6	1363	-1379
3	6	764	764
4	6	324	256
5	6	407	-443
-3	7	290	286
-2	7	572	-525
-1	7	1430	1423
0	7	461	-446
1	7	519	486
2	7	916	879
5	7	474	456
-2	8	329	-303
-1	8	267	265
0	8	236	-216
1	8	261	-226
3	8	267	200
5	8	259	244
-3	10	282	269
-2	10	503	-487
0	10	621	660
1	10	267	-294
2	10	380	-350
3	10	688	710
-1	11	599	639
0	11	408	-385
1	11	320	330
2	11	249	251
-1	12	429	475
0	12	274	-265
2	12	578	594
K = 3			
1	0	1692	1587
2	0	178	-204
3	0	699	-669
4	0	947	926
5	0	265	254
6	0	456	-439
7	0	411	427
-4	1	1190	1235
-2	1	1547	1503
-1	1	657	640
0	1	1482	1515
1	1	256	-233
2	1	1714	1702
3	1	183	-127
4	1	657	727
5	1	291	-227
-5	2	830	-808
-4	2	623	614
-3	2	500	450
-2	2	1302	-1281
-1	2	1635	1546
0	2	941	980
1	2	1379	-1379
2	2	1062	1037
3	2	375	376
5	2	371	353
-4	3	694	719
-2	3	1221	1281
0	3	1521	1525
1	3	402	404
2	3	1006	1022
3	3	613	-645
4	3	722	779
5	3	366	-355
-6	4	331	309
-5	4	407	-407
-3	4	512	456
-2	4	185	-152
-1	4	300	-280
0	4	492	514
1	4	402	361
4	4	980	811
7	4	439	405
-5	5	239	193
-4	5	808	808
-2	5	999	965
-1	5	533	518
0	5	550	589
1	5	399	-362
2	5	1023	1037
3	5	329	-336
4	5	344	347
5	5	374	-397
-5	6	542	-572
-4	6	939	983
-2	6	1072	-1040
-1	6	1351	1377
0	6	574	566
1	6	1299	-1351
2	6	1344	1299
3	6	578	590
4	6	410	-445
5	6	291	231
6	6	435	445
-5	7	257	225
-2	7	769	794
0	7	299	290
1	7	161	120
2	7	239	239
3	7	679	-709
4	7	394	341
5	7	395	-382
-4	8	335	337
-1	8	477	481
2	8	741	680
3	8	279	-301
5	8	249	211
-2	10	204	-151
-1	10	669	756
1	10	425	-510
2	10	751	813
4	10	341	-254
-2	11	325	241
2	11	283	-161
3	11	503	-382
0	12	314	-366
1	12	474	421
2	12	298	285
K = 4			
0	0	226	-183
1	0	1059	1052
2	0	1297	-1341
3	0	1160	1188
5	0	313	-329
7	0	398	445
8	0	241	-211
-6	1	304	289
-4	1	806	773
-2	1	268	252
-1	1	598	584
0	1	573	-591
1	1	669	-679
2	1	380	384
3	1	353	-426
4	1	800	-838
6	1	464	-487
-6	2	360	-432
-4	2	457	477
-3	2	377	-385
-2	2	687	-632
-1	2	1494	1558
0	2	2012	-2082
1	2	1161	1198
2	2	200	-207
3	2	180	167
4	2	206	-198
5	2	298	330
-6	3	341	328
-4	3	543	485
0	3	219	-174
1	3	873	-879
2	3	397	-436
3	3	746	-663
4	3	756	-732
5	3	279	-231
6	3	490	-480
7	3	258	-158
-4	4	334	324
-2	4	753	-756
-1	4	1395	1396
0	4	439	-439
1	4	507	534
2	4	729	-655
3	4	918	936
4	4	267	-291
-4	5	281	284
-3	5	629	-599
0	5	876	-948
1	5	747	-733
3	5	950	-996
4	5	575	-587
6	5	390	-455
-5	6	427	449
-3	6	905	-885
-2	6	358	338
-1	6	1078	1098
0	6	1911	-2043
1	6	881	910
2	6	345	326
3	6	350	-326
4	6	271	-251
5	6	550	562
6	6	306	-239
-5	7	273	-246
-3	7	234	-183
-2	7	198	-182
-1	7	514	-547
1	7	486	-519
2	7	384	-419
3	7	527	-499
6	7	300	-293
0	8	497	-467
1	8	775	797
2	8	547	-482
3	8	195	185
5	8	163	96
-3	10	314	-400
-2	10	421	403
-1	10	251	163
0	10	747	-827
1	10	725	703
3	10	333	-386
-1	11	327	-333
1	11	322	-260
K = 5			
1	0	1172	-1180
2	0	1012	1037
3	0	469	461
4	0	293	-272
6	0	558	605
7	0	250	-282
-4	1	287	-232
-3	1	1172	-1201
-2	1	351	374
-1	1	926	-905
0	1	1866	-1941
1	1	265	238
2	1	555	-589
3	1	1387	-1459
4	1	560	560
5	1	336	-326
6	1	306	-284
-6	2	454	-440
-5	2	509	485
-4	2	610	-565
-3	2	222	-203
-2	2	414	395
-1	2	227	233
0	2	665	-683
1	2	717	723
2	2	369	385
4	2	271	309
-6	3	299	-241
-5	3	365	-377
-3	3	1280	-1246
-2	3	440	-372
-1	3	242	-261
0	3	981	-993
3	3	812	-806
-6	4	390	-400
-5	4	256	278
-2	4	392	-447
-1	4	747	753
0	4	558	-532
2	4	563	665
4	4	249	-226
5	4	311	356
-3	5	663	-733
-2	5	553	485
-1	5	802	-795
0	5	951	-1017
1	5	626	592
2	5	495	-489
3	5	716	-655
4	5	725	736
5	5	289	-253
-5	6	509	449
-4	6	784	-813
-3	6	227	169
-2	6	531	541
-1	6	228	-197
0	6	539	-605
1	6	1317	1358
2	6	326	-355
3	6	266	-368
4	6	531	578
-3	7	543	-577
-2	7	226	-143
-1	7	242	-203
2	7	225	-198
4	7	357	283
1	10	719	658
2	10	486	-516
4	10	328	290
K = 6			
0	0	836	-882
1	0	771	750
2	0	1514	1576
3	0	1213	-1209
4	0	489	494
5	0	462	426
6	0	318	-261
-4	1	237	-221
-2	1	409	405
-1	1	888	-936
0	1	636	603
1	1	464	530
2	1	676	-736
3	1	811	857
4	1	466	489
6	1	250	238
7	1	275	267
-2	2	951	962
-1	2	400	-360
0	2	429	433
1	2	544	560
2	2	327	313
3	2	410	-451
4	2	641	692
5	2	277	-240
-3	3	295	-309
-2	3	850	847
-1	3	582	-549
0	3	344	339
1	3	721	732
3	3	336	361
4	3	307	296
7	3	284	164
-5	4	362	318
-3	4	263	-245
-2	4	1272	1286
0	4	246	-220
1	4	862	890
2	4	490	522
3	4	991	-1013
4	4	727	720
6	4	303	-339
-3	5	222	161
-2	5	251	247
-1	5	424	-463
0	5	1176	1179
2	5	229	-275
3	5	857	867
4	5	319	334
6	5	445	402
-3	6	469	438
-1	6	625	-604
0	6	745	726
1	6	241	202
2	6	553	-541
4	6	494	476
5	6	722	-739
-2	7	554	646
0	7	393	372
2	7	418	385
3	7	268	288
5	7	217	178
0	10	303	330
1	10	213	-143
2	10	258	-271
3	10	237	115
K = 7			
1	0	1247	1300
2	0	1467	-1485
3	0	195	-195
4	0	336	363
5	0	497	-495
6	0	316	-354
-7	1	269	258
-3	1	470	523
-2	1	569	-600
-1	1	1220	1283
0	1	180	-134
3	1	916	893
4	1	354	-335
5	1	313	344
-2	2	432	394
-1	2	780	-773
0	2	303	300
2	2	992	-1111
3	2	242	211
4	2	306	-297
5	2	451	-505
-5	3	267	305
-3	3	448	468
-1	3	528	519
0	3	265	-303
1	3	913	988
2	3	264	-280
3	3	493	510
-2	4	410	372
-1	4	1158	-1239
0	4	429	456
1	4	224	207
2	4	1384	-1429
3	4	282	303
5	4	599	-655
-4	5	249	261
-3	5	227	205
-2	5	284	-332
-1	5	851	859
0	5	329	-294
0	5	307	-294
3	5	511	520
4	5	467	-526
-1	6	229	-211
0	6	282	299
1	6	680	-740
2	6	511	-560
3	6	381	383
4	6	621	-622
5	6	214	-254
0	7	445	-456
1	7	488	603
2	7	246	-233
1	10	304	-408
K = 8			
0	0	1049	1067
1	0	1105	-1197
2	0	617	-622
5	0	420	-481
-6	1	359	-361
-5	1	413	463
-3	1	372	-336
-2	1	310	326
0	1	521	-520
1	1	238	263
-3	2	472	-498
-2	2	362	-418
-1	2	567	-504
1	2	1167	-1199
-4	3	491	-481
-1	3	351	-361
0	3	195	128
1	3	244	269
2	3	489	-512
5	3	312	-311
-5	4	334	-334
-2	4	390	-394
-1	4	460	-484
0	4	560	541
1	4	999	-1047
4	4	304	-265
-4	5	461	-412
-2	5	258	237
0	5	472	-479
1	5	404	417
-3	6	534	-565
0	6	222	-224
1	6	598	-575
2	6	566	615
3	6	372	-332
5	6	258	293
-3	7	344	364
-1	7	390	-440
1	7	292	313
2	7	635	-680
K = 9			
1	0	251	-241
2	0	237	215
4	0	286	-208
6	0	239	189
-4	1	459	-518
-3	1	357	352
-2	1	391	369
-1	1	506	-539
0	1	460	507
-3	2	417	-436
-2	2	389	349
1	2	281	267
6	2	239	129
-3	3	338	296
-2	3	191	-144
0	3	511	549
1	3	468	-459
2	3	268	246
4	3	351	-333
-2	4	377	390
2	4	447	488
5	4	386	336
-4	5	316	-344
-3	5	524	561
-1	5	422	-440
0	5	491	521
2	5	208	-178
-2	6	604	640
-1	6	327	-330
0	6	249	189
1	6	520	524
4	6	475	406
-3	7	304	322
-2	7	330	-395
-1	7	233	172
0	7	422	474
1	7	467	-555
3	7	222	195
K = 10			
1	0	390	389
2	0	182	147
3	0	355	359
5	0	347	388
-6	1	230	261
-3	1	443	475
0	1	309	348
2	1	373	-373
6	1	237	-134
-4	2	274	-279
-3	2	641	634
0	2	275	298
1	2	286	265
3	2	502	471
5	2	318	235
3	3	250	-247
-3	4	487	488
1	4	363	315
3	4	262	260
-3	5	343	307
-2	5	281	-325
1	5	229	-240
-3	6	481	519
-2	6	266	-265
0	6	412	433
2	6	418	416
0	7	296	-307
K = 11			
3	0	338	-321
4	0	253	199
-5	1	279	-276
-2	1	295	-290
-1	1	241	-242
0	1	414	426
1	1	746	-773
-3	2	276	292
-2	2	513	-529
-1	2	222	203
1	2	255	-267
-1	3	412	-410
0	3	265	256
1	3	373	-381
-2	4	371	-383
-2	5	233	-218
1	5	607	-618
2	5	342	316
-2	6	446	-470
-1	6	382	349
1	6	293	-313
K = 12			
-2	1	286	-253
-1	1	408	423
0	1	299	-226
1	1	264	-239
2	1	488	555
5	1	357	360
-1	3	256	246
2	3	362	366
5	3	266	238
-1	5	281	258
0	5	238	-209
2	5	492	492
K = 13			
1	0	291	-318
2	0	247	205
-5	1	267	123
-1	1	233	143
0	1	282	-310
1	1	553	532
-1	2	324	262
0	2	234	-134
2	2	255	216
1	3	305	267
K = 14			
0	0	271	-256
2	0	248	174
3	0	263	-294
0	2	352	-218
4	2	255	186

Table 4. *Interatomic distances and angles*

(*a*) $FeBr_4$ anion

	d	$d_{corr.}$	Angle	
Fe—Br(1)	2·309 (4) Å	2·328 (4)	Br(1)–Fe–Br(2)	110·9 (2)°
Fe—Br(2)	2·324 (4)	2·347 (4)	Br(1)–Fe–Br(3)	109·3 (2)
Fe—Br(3)	2·326 (4)	2·351 (4)	Br(1)–Fe–Br(4)	107·7 (2)
Fe—Br(4)	2·345 (4)	2·362 (4)	Br(2)–Fe–Br(3)	110·5 (2)
Br(1)–Br(4)	3·757 (4)	– –	Br(2)–Fe–Br(4)	109·0 (2)
Br(2)–Br(3)	3·821 (4)	– –	Br(3)–Fe–Br(4)	109·4 (2)

(*b*) $C_7H_9NH^+$ cation

C–N	1·340 Å	C(6)–N(1)–C(2)	117·0
C–C	1·394	N(1)–C(2)–C(3)	123·7
N–H	1·050	N(1)–C(6)–C(5)	123·7
C–H	1·080	C(2)–C(3)–C(4)	118·5
C(4)–C(7)	1·540	C(6)–C(5)–C(4)	118·5
C(7)–C(8)	1·073	C(3)–C(4)–C(5)	118·5
		C(4)–C(7)–C(8)	129·6

(*c*) Other

Br(4)–H(1)	2·330 Å	Br(4)–H(1)–N(1)	156·9
Br(4)–N(1)	3·321	Fe—Br(4)–H(1)	114·7
$Br(1)–Br(1)_i$	3·724 (5)	Fe—Br(4)–N(1)	107·6
$Br(4)–Br(1)_{ii}$	3·998 (4)		

(i) $\bar{x}$, $\bar{y}$, $\bar{z}$
(ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$

motion, using a riding-model approximation. The shortest bromine---bromine contact within the group is 3·76 Å. All bond distances and angles are listed in Table 4 (see Fig. 1). Ring atoms of the 4-ethylpyridinium cation were fixed in the rigid-body refinement. The unusually short C(7)–C(8) distance obtained in the ethyl group is a result of the large thermal parameters associated with those atoms. Using the anisotropic thermal parameters obtained from the earlier refinement, this distance adjusts to 1·51 Å when a riding model is assumed. The high thermal motion of the cation can be attributed to the size of its cavity.

A unit-cell drawing of 4-ethylpyridinium tetrabromoferrate(III) is shown in Fig. 2. The $FeBr_4^-$ tetrahedra are nearly aligned with their threefold axes almost coincident in the **c** direction. The closest bromine---bromine distance in this direction is 4·00 Å, which is greater than the sum of the van der Waals radii of 3·90 Å. The shortest intermolecular bromine---bromine distance is 3·72 Å involving Br(1) across a center of symmetry. One significantly short hydrogen---bromine distance involving H(1) and Br(4) of 2·3 Å is present. The Fe–Br(4)---H(1) and Br(4)---H(1)–N(1) angles are 115 and 157°, respectively. The Fe–Br(4) bond distance is also slightly longer than the other Fe–Br distances. The N–H---Br(4) hydrogen bond may contribute to the slight ion deformation and the crystal stability of this compound.

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On the Crystal Structure of B_2O_3

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The crystal structure of B_2O_3 derived by Gurr, Montgomery, Knutson & Gorres is not essentially different from that reported earlier by Strong & Kaplow. Removal of an arbitrary transformation of axes shows the newer single-crystal results to be a refinement (associated with inequalities in the near-neighbor separation distances) which is verified by the original powder data and the atomic pair distribution fitting procedure.

Two of the present authors have previously published a description of the structure of crystalline B_2O_3 (Strong & Kaplow, 1968; hereafter referred to as SK). That description was based on analysis of the radial pair-distribution function, $4\pi r[\varrho(r)-\varrho_o]$, determined from the Fourier transform of the reduced X-ray intensities recorded from powder specimens. The reduced intensity is defined as:

$$k\{[I(k)-\langle f^2\rangle]/\langle f\rangle^2\},$$

where: $k=4\pi \sin\theta/\lambda$

$I(k)$ = intensity, electron units

$\langle f\rangle=\sum x_i f_i(k)$

$f_i(k)$ = atomic scattering factor, ith element

x_i = atomic fraction, ith element

$4\pi r^2\varrho(r)\mathrm{d}(r)$ = number of atoms in a spherical shell of radius r and thickness $\mathrm{d}r$ about an average atom, each pair-type being weighted by its scattering power.

ϱ_o = mean number of atoms per unit volume.