

It may be noted that the only polyhedra in phase III similar in shape to those reported in phase IV are Pb4 F₉ and Pb5 F₉; these are also the only two polyhedra with all Pb—F distances greater than about 2.5 Å. The three other polyhedra each have one short Pb—F distance, 2.36 (4) Å for Pb1, 2.29 (4) Å for Pb2 and 2.25 (4) Å for Pb3. Bond overlap with the lone pair is expected to reduce the Pb—F distance. It may also be noted that the short Pb—F distances in the Pb2 and Pb3 polyhedra are directed toward capping atoms. Direct determination by X-ray diffraction of the lone-pair orientation in these Pb compounds requires a structure-factor accuracy no less than about 1%, an achievement that will become possible with the growth of larger and higher quality crystals. Investigation of the Pb₅Al₃F₁₉ structure in the remaining phases, now in progress, may contribute further to understanding the rôle of the Pb lone pair.

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Space Group of the Trirutile Type Structure of Li₂MoF₆

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Abstract

Dilithium molybdenum hexafluoride, Li₂MoF₆, tetragonal, $M_r = 223.83$, $a = 4.6863$ (7), $c = 9.191$ (2) Å, $V = 201.8$ (2) Å³, $D_x = 3.683$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 206$, single crystal refinement to $R = 0.057$ in space group $P4_2/m2_1/n2/m$ based on 371 structure factors measured on a diffractometer by Brunton [(1971). *Mater. Res. Bull.* **6**, 555] who preferred in his refinement of the same data space group $P4_22_12$. Refinements in space groups $P4_2$, $P4_22_12$ and $P4_2/m2_1/n2/m$ show that Li₂MoF₆ crystallizes in the most highly symmetric of these space groups and is, therefore, isostructural with the aristotypic trirutile type. The decision for space group $P4_2/m2_1/n2/m$ is based on the shape and orientation of the displacement ellipsoid of the F(1) atom and on the extremely high R value of the reflections not obeying the extinction condition of the n glide in space group $P4_22_12$. The importance of the weak reflections in deciding a centrosymmetric–non-centrosymmetric space-group ambiguity is emphasized.

Introduction

The crystal structure of rutile, one of the three naturally occurring polymorphs of TiO₂, was determined by Vegard (1916). Goldschmidt (1926) determined the crystal structures of the minerals mossite, Fe(Nb,Ta)₂O₆, and tapiolite, FeTa₂O₆. They crystallize in a superstructure of the rutile type, which could be derived by a tripling of the c cell constant. The space group type was the same as for rutile, $P4_2/m2_1/n2/m$, and the cations were distributed in an ordered way over the octahedrally coordinated cation positions, thus generating the superstructure. Goldschmidt (1926) coined the term trirutile for this arrangement. This structure type has been identified in a variety of oxides and fluorides, in which mostly two different octahedrally coordinated cations occur in a ratio of 2:1 (AB_2X_6). The trirutile type is best defined narrowly as a derivative of rutile, with a tripled c cell constant and space group $P4_2/m2_1/n2/m$ (Baur, 1994). In the case of this space group, the maximal isomorphic *klassengleich* subgroup of the lowest index is of

Table 1. Results of different refinements of Li₂MoF₆

$R = \sum(|F_o| - |F_c|) / \sum|F_o|$; $wR = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$; total number of F_o used in refinement: $\#F_o$; number of structure factors contained in $\#F_o$ assumed to be zero: $\#F_o = 0.0$; number of variables: $\#V$; goodness of fit: GoF; largest observed absolute value of correlation coefficients between refined parameters: highest cc. All refinements were performed with unit weights.

Space group	R	wR	$\#F_o$	$\#F_o = 0.0$	$\#V$	GoF	Highest		Remarks
							cc	cc	
(1) $P4_2/m2_1/n2/m$	0.057	0.058	371	45	16	1.429	0.59		
(2) $P4_22_12$	0.066	0.064	420	66	20	1.485	0.59		
[Group 1:	0.056		371	45	w/o $F_{0kl}(k+l=2n+1)$, $F_{mean} = 17.8$				
[Group 2:	0.756		49	21	for $F_{0kl}(k+l=2n+1)$, $F_{mean} = 1.9$				
(3) $P4_22_12$	0.055	0.055	371	45	20	1.376	0.83		
(4) $P4_22_12$	0.041	0.045	326	0	20	1.208	0.58	w/o $\#F_o = 0.0$	
(5) $P4_2$	0.079	0.071	424	68	18	1.667	0.86		Isotropic displacement parameter
(6) $P4_2$	0.067	0.063	424	68	36	1.496	0.88		Anisotropic displacement parameter

index 3 (*International Tables for Crystallography*, 1983, Vol. A).

Tetragonal trirutile type related structures of lower symmetry are in principle possible. However, when Viebahn & Epple (1976) synthesized a number of $LiM^{2+}M^{3+}F_6$ compounds these were found to crystallize in the trirutile type in space group $P4_2/m2_1/n2/m$; that is the cations were not completely ordered, but instead statistically distributed over the two cation sites available in this case. A new investigation (Aruga, Tokizaki, Nakai & Sugitani, 1985) of the synthetic counterpart of mossaite, $FeNb_2O_6$, showed it to crystallize in $P4_21m$, a *translationengleich* maximal subgroup of $P4_2/m2_1/n2/m$. Even though the ratio of Fe to Nb is overall 1:2, there are apparently three crystallographically distinct cation sites in this structure, each with a different Fe:Nb ratio. Brunton (1971) described the crystal structure of Li_2MoF_6 in space group $P4_22_12$. Since another compound of tetravalent Mo (MoO_2 , Magnéli & Andersson, 1955, with apparent Mo—Mo bonding across the common edge of the coordination octahedra around Mo) shows a monoclinic distortion $P2_1/n$ of the rutile-type structure the present case of a possibly lower symmetry should be looked into more closely. Brunton (1971) reports reflections violating the extinction condition of the glide plane n (F_{0kl} observed for $k+l=2n+1$).

Refinements

Brunton (1971) lists 424 F_{hkl} in Table 1 of his paper. They were measured on an automatic diffractometer. For details of data collection see Brunton's (1971) original paper. Of the 424 F_{hkl} listed, four are of the type F_{h00} with $h=2n+1$, that is they violate the assumption that the space group of Li_2MoF_6 has a 2_1 axis parallel [100] (of these four reflections, two were assumed to have zero intensity). An additional 49 F_{hkl} listed by Brunton are of the type F_{0kl} with $k+l=2n+1$, that is they violate the assumption that the space group of Li_2MoF_6 has an n -glide normal on [100] (of these 49 reflections 21 were

assumed to be of zero intensity). Thus, the most likely space groups for Li_2MoF_6 should be either $P4_222$ or $P4_2$. The amplitudes of the observed structure factors for the reflections violating either the assumption of a twofold screw axis or of the n -glide plane are reported to lie between 10 and 54, where the value for F_{100} is 29 and for F_{500} it is 47. The proper space group of Li_2MoF_6 according to this evidence would have to be $P4_2$, because $P4_222$ is not a subgroup of space group $P4_22_12$.

However, the refinements of all 424 structure factors in space group $P4_2$ yielded R values higher than those in $P4_2/m2_1/n2/m$, the space group of trirutile itself (Table 1, lines 5 and 6). In addition, high correlation coefficients were encountered for pseudo-symmetrically related parameters. The refinement had difficulties in converging and in the refinement with anisotropic displacement factors, a non-positive definite matrix occurred for the displacement parameters of one of the atoms derived from F(1). But most significantly, the agreement of the observed and calculated structure factors F_{h00} was exceedingly poor (R values of 1.15 and 0.85).

Since the measurements of the intensities of the reflections F_{h00} thus appear to be spurious, it appears that the observations of the F_{0kl} are equally irrelevant (they are of the same magnitude). However, since Brunton (1971) reported a successful refinement in space group $P4_22_12$, a refinement in that space group was performed as well. A least-squares refinement of the 420 F_{hkl} yielded R values clearly higher than for the aristotype of trirutile in space group $P4_2/m2_1/n2/m$ (see Table 1, line 2 for R values and Table 2 for parameters) and there were no high correlation coefficients between related parameters. When the structure factors are divided into two groups, those obeying the reflection conditions for the n glide and those violating it, group 1 has R values slightly lower than for the refinement in $P4_2/m2_1/n2/m$, while group 2 has an R value higher than statistically expected for a random arrangement of atoms in a non-centrosymmetric space group ($R = 0.586$, Wilson, 1950). Since these are exactly the

Table 2. Atomic positional coordinates and isotropic and anisotropic displacement parameters U_{iso} , U_{eq} and U_{ij} (\AA^2) of Li_2MoF_6 in space groups $P4_2/m2_1/m2/m$ (A) and in $P4_22_12$ (B)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	Wyckoff position	Site symmetry	x	y	z	U	
Mo	A	2(a)	0	0	0	0.0126 (2)†	
	B	2(a)	0	0	0	0.0126 (2)†	
Li	A	4(e)	0	0	0.337 (2)	0.022 (3)	
	B	4(c)	0	0	0.337 (2)	0.022 (3)	
F(1)	A	8(j)	0.3052 (6)	x	0.3424 (4)	0.0138 (6)†	
	B	8(g)	0.2955 (12)	0.3123 (10)	0.3426 (4)	0.013 (1)†	
F(2)	A	4(f)	0.2909 (8)	x	0	0.0133 (8)†	
	B	4(e)	0.2909 (8)	x	0	0.0135 (9)†	
Mo	A	U11	U22	U33	U12	U13	U23
	B	0.0135 (2)	U11	0.0107 (3)	0.0006 (3)	0	0
F(1)	A	0.0136 (3)	U11	0.0107 (3)	0.0003 (3)	0	0
	B	0.0150 (9)	U11	0.012 (1)	-0.002 (1)	-0.0036 (8)	U13
F(2)	A	0.021 (2)	0.007 (2)	0.011 (1)	-0.002 (1)	-0.007 (2)	-0.000 (1)
	B	0.012 (1)	U11	0.017 (2)	-0.002 (2)	0	0
F(1)	A	0.012 (1)	U11	0.017 (2)	-0.004 (2)	-0.001 (2)	-U13
	B	0.012 (1)	U11	0.017 (2)	-0.004 (2)	-0.001 (2)	-U13
Root-mean-square thermal displacement along the principal axes (\AA) of F(1)							
A	0.08	0.13	0.13				
B	0.08	0.09	0.16				

† U_{eq} values.

structure factors which should prove the non-centrosymmetric deviation of the superstructure from the aristotypic substructure in space group $P4_2/m2_1/n2/m$, it seems that the higher symmetry should in this case be the correct one, because there is no proof from the refinement for any of the lower symmetries. Therefore, the structure was refined in $P4_2/m2_1/m2/m$ using 371 structure factors* (Table 1, line 1; Table 2).

All the refinements reported here were performed with unit weights, since no σ values were listed in Brunton (1971). The scattering factors and dispersion corrections for Li^+ , Mo^{3+} and F^- were taken from the *International Tables for X-ray Crystallography* (1974, Vol. IV). The following programs were used in this work: for the least-squares refinements, *CRYLSQ* (Olthof-Hazekamp, 1990); for the distance and angle calculations, *SADIAN90* (Baur & Kassner, 1991); for the drawing of the structure, *ATOMS* (Dowty, 1993); for the plotting of the displacement ellipsoids, *ORTEP* (Davenport, Hall & Dreissig, 1990).

Discussion

The results of the refinement of the diffraction data of Li_2MoF_6 in three different space groups

* Lists of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71661 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England. [CIF reference: SH0038]

($P4_2/m2_1/n2/m$, $P4_22_12$ and $P4_2$) show that a meaningful refinement, in terms of R values, correlation coefficients and/or anisotropic displacement parameters, is only possible in the most highly symmetric space group. Thus, Li_2MoF_6 crystallizes after all in the aristotypic trirutile type structure. The bond lengths and bond angles around the Mo, Li and F atoms conform with the expected values (Table 3) [as they did in the original crystal structure determination by Brunton (1971)] when compared with the appropriate ionic radii (Müller, 1993). On the basis of the bond lengths and angles alone it would be difficult to decide in which space group Li_2MoF_6 should best be described. However, a look at the structure (Fig. 1) and at the displacement ellipsoids (Fig. 2, Table 2) resulting from the refinements in space groups $P4_2/m2_1/n2/m$ and $P4_22_12$ allows a clear cut decision. In the higher symmetry, the oblate displacement ellipsoids of F(1) are arranged with their two long axes at right angles to the vector Mo—F, as expected for the thermal movement of a strongly bound MoF_6 molecule. In space group $P4_22_12$ the prolate displacement ellipsoid of F(1) makes an awkward skewed angle with the vector Mo—F. Interestingly, the distance from the location of F(1) in space group $P4_22_12$ to F(1) on the diagonal mirror plane in $P4_2/m2_1/n2/m$ is only 0.056 \AA . Thus, the location of the former atom is well within the displacement ellipsoid of the latter atom (compare the values of the r.m.s. axes in Table 2).

Table 3. Li₂MoF₆ bond lengths (Å) and bond angles (°) in space groups $P4_2/m2_1/n2/m$ (A) and $P4_22_12$ (B)

	A	B		A	B
2 × Mo—F(2)	1.928 (4)	1.928 (4)	2 × Li—F(1)	2.023 (3)	2.016 (5)
4 × Mo—F(1)	1.940 (3)	1.946 (4)	2 × Li—F(2)	2.04 (1)	2.04 (1)
Mean	1.936	1.940	2 × Li—F(1)	2.09 (1)	2.10 (2)
			Mean	2.051	2.052
	A	B		A	B
F(2)—Mo—F(2)	180.0 (2)	180.0 (2)	F(1)—Li—F(1)	177.2 (10)	177.1 (11)
F(1)—Mo—F(1)	180.0 (2) (2 ×)	176.7 (2) (2 ×)	F(1)—Li—F(2)	89.0 (4) (4 ×)	90.0 (4) (2 ×)
F(2)—Mo—F(1)	90.0 (1) (8 ×)	91.6 (2) (4 ×)			87.9 (4) (2 ×)
			F(1)—Li—F(1)	91.1 (4) (4 ×)	90.6 (4) (2 ×)
F(1)—Mo—F(1)	96.6 (1) (2 ×)	96.2 (2) (2 ×)			91.7 (5) (2 ×)
F(1)—Mo—F(1)	83.4 (1) (2 ×)	83.9 (2) (2 ×)	F(2)—Li—F(2)	85.5 (7)	85.6 (7)
			F(2)—Li—F(1)	99.2 (1) (2 ×)	99.0 (2) (2 ×)
			F(2)—Li—F(1)	175.3 (7) (2 ×)	175.2 (6) (2 ×)
			F(1)—Li—F(1)	76.1 (6)	76.5 (7)

It is remarkable that the correlation coefficients between the pseudo-symmetrically related parameters in space group $P4_22_12$ [that is x and y , U_{11} and U_{22} , U_{13} and U_{23} of F(1)] are not larger than they

are found to be (around -0.48). Usually, one expects singular matrices (or at least extremely high correlation coefficients) in the least-squares refinement when a really centrosymmetric crystal structure is refined falsely in a non-centrosymmetric space group (Schomaker & Marsh, 1979). In the present case, this is apparently dampened by the presence in the refinement of the 49 structure factors violating the n -glide plane since the correlation

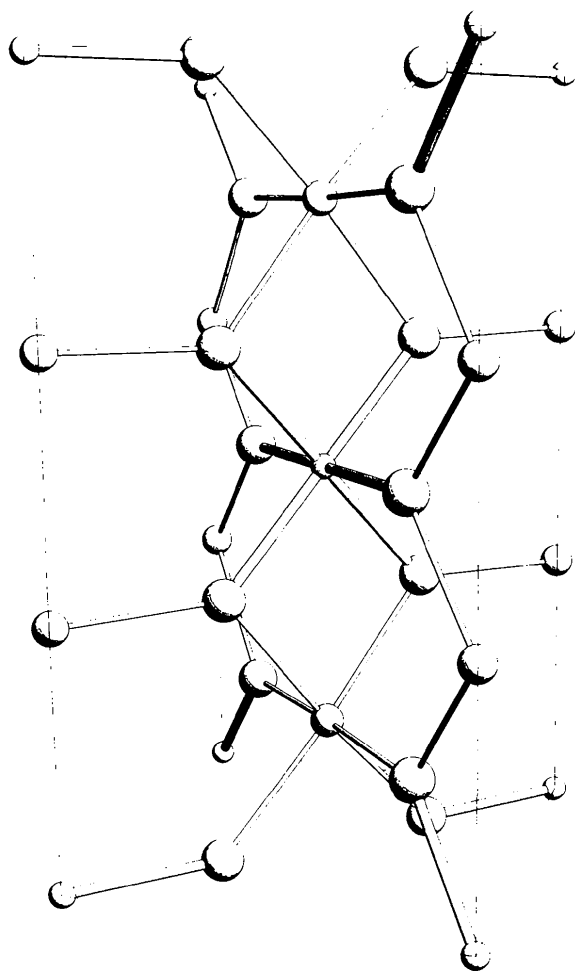


Fig. 1. Unit cell of Li₂MoF₆ (in space group $P4_2/m2_1/n2/m$), [001] points up, large-sized spheres represent fluorine, medium-sized spheres lithium and the smallest molybdenum. Thick connections represent the Mo—F bonds, thin connections the Li—F bonds. Drawing produced using *ATOMS* (Dowty, 1993).

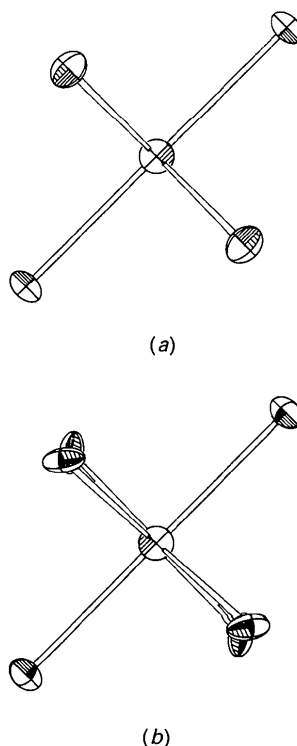


Fig. 2. Displacement ellipsoids within the MoF₆ molecule of Li₂MoF₆ in space group $P4_2/m2_1/n2/m$ (a) and in space group $P4_22_12$ (b). The view is parallel to [001]. The two apical bonds within the plane of the drawing represent Mo—F(2) along the diagonal [110]. The four equatorial bonds completing the octahedron correspond to the Mo—F(1) bonds. Drawing produced using *ORTEP* (Davenport, Hall & Dreissig, 1990).

matrix is determined by the partial derivatives, not by the goodness of fit. Even though the agreement between observation and calculation is very poor for these reflections, their presence alone inhibits the occurrence of strong correlations between related parameters. In a refinement in space group $P4_22_12$, without including the reflections not obeying the n -glide condition, the correlation coefficients exceed 0.8 (Table 1, line 3), but a singular matrix still does not occur. This is similar to the case of $C_8H_{20}N_2 \cdot 2HBr$ discussed by Baur & Tillmanns (1986), where the refinement in space group $Pba2$ of a structure crystallizing in space group $Pbam$ did not result in a singular matrix. The reason is apparently the same as in the case of Li_2MoF_6 : the removal of the inversion centre does not split two centrosymmetrically related sites into two independent sites, but instead changes a special position located on a mirror plane into a general position. The instance of centrosymmetrically related pairs of parameters leading to structure-factor derivatives equal in magnitude, but of opposite sign, causing the singular matrix (Ermer & Dunitz, 1970), does not occur here.

A refinement in space group $P4_22_12$ based on 326 F_{hkl} , that is on all reflections obeying the reflection condition of the n -glide, but omitting the 45 structure factors observed with zero intensity shows reduced correlation coefficients between related parameters (Table 1, line 4) and the value of R is 0.041. This result agrees with the suggestion of Schomaker & Marsh (1979) to be sure to keep the weak reflections in the least-squares refinement when trying to decide between the presence or absence of an inversion centre. In this case, it is apparently more diagnostic to keep the zero intensities than to disregard them. This point was made experimentally recently by Kassner *et al.* (1993) when trying to decide the question of the correct space group of margarite (Cc versus $C2/c$). For margarite, the inclusion of the weak reflections lowered the correlation coefficients, since the true space group was without an inversion centre (Cc), while for Li_2MoF_6 the inclusion of the weak reflections (the zero intensities) raises the correlation coefficients because the true space group is centrosymmetric.

Since the compound contains Mo, which has with Mo $K\alpha$ radiation appreciably large values of f' and f'' , a check of the correct space group should have been made by comparing the intensity of each F_{hkl} with the intensity of its Friedel mate (see Kassner *et al.*, 1993). However, Brunton (1971) did not report the separate measurement of Friedel pairs.

This is the second case of a reported space-group revision from $P4_22_12$ to $P4_2/m2_1/n2/m$ (see entry 194 in Table 1 and Table 2 in Baur & Kassner, 1992).

Concluding remarks

Li_2MoF_6 crystallizes in space group $P4_2/m2_1/n2/m$ and is, therefore, strictly isotopic with the aristotypic trirutile type structure, despite the presence of tetravalent Mo, which displays in some other compounds interesting stereochemical features (MoO₂, Magnéli & Andersson, 1955). This must be because of the different pattern of distribution of Mo atoms in the framework of trirutile as compared with the distorted rutile-type structure of MoO₂. Interactions between neighbouring Mo atoms are not possible in Li_2MoF_6 because the individual MoF₆ octahedra are completely separated from each other by intervening LiF₆ octahedra (Fig. 1). No F atoms are bonded simultaneously to two Mo atoms.

When trying to resolve a centrosymmetric–non-centrosymmetric space-group ambiguity (in a case where the higher symmetry is the correct choice), inclusion into the least-squares calculation of spurious measurements of reflections apparently violating a reflection condition tends to support the choice of the lower symmetry option. However, on the other hand, the inclusion of weak reflections, even if they happen to be extremely weak (that is of zero intensity), improves the chances of deciding the case for the higher symmetry.

Note added in proof: When writing this manuscript I had overlooked a case of a lower symmetry described for a trirutile type related compound. In $LiFe^{2+}Fe^{3+}F_6$ (Fourquet, LeSamedi & Calage, 1988), all three cations are ordered and located on separate equivalent positions according to the symmetry of space group $P4_2nm$. The lower symmetry in this case is based on the diffraction evidence and on the requirements of the chemical composition of the compound. In the case of Li_2MoF_6 , there is no crystal chemical reason for a lower symmetry and originally the diffraction evidence was taken into account only incompletely.

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Structures of (Ferrocenylmethyl)trimethylammonium Iodide and Hexa-*N*-methylferrocene-1,1'-diylbis(methylammonium Iodide)

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Abstract

(Ferrocenylmethyl)trimethylammonium iodide (1), [C₁₄H₂₀FeN][I], *M_r* = 385.07, monoclinic, *P*2₁/*c*, *a* = 8.6236 (5), *b* = 13.5926 (10), *c* = 12.8623 (6) Å, β = 102.792 (4)°, *V* = 1470.3 (2) Å³, *Z* = 4, *T* = 293 K, *F*(000) = 760, *D_x* = 1.74 g cm⁻³, *Mo Kα*, λ = 0.71069 Å, μ = 3.08 mm⁻¹, *R* = 0.024 for 4075 observations [*I* > 3σ(*I*)]. The [(C₅H₅)Fe(C₅H₄)-CH₂N(CH₃)₃]⁺ cation is involved in a three-dimensional network of C—H···I⁻ interactions (both the cation and anion residing in general positions). The shortest C···I distances are 3.954 (2), 3.992 (2) and 4.009 (3) Å. Hexa-*N*-methylferrocene-1,1'-diylbis(methylammonium iodide) (2), [C₁₈H₃₀FeN₂].2[I], *M_r* = 584.10, monoclinic, *C*2/*c*, *a* = 27.1457 (12), *b* = 12.3446 (6), *c* = 14.5295 (10) Å, β = 115.909 (4)°, *V* = 4379.5 (4) Å³, *Z* = 8, *T* = 293 K, *F*(000) = 2264, *D_x* = 1.772 g cm⁻³, *Mo Kα*, λ = 0.71069 Å, μ = 3.48 mm⁻¹, *R* = 0.031 for 4482 observations [*I* > 3σ(*I*)]. In (2), the [Fe{(C₅H₄)CH₂-N(CH₃)₃}₂]²⁺ cation (which has approximate twofold symmetry) and one of the anions reside in general positions. Another iodide resides on a twofold axis, while a third iodide lies on an inversion centre. A more extensive three-dimensional network of C—H···I⁻ interactions is present in (2) than in (1) and

involves all three of the iodide anions. The shortest C···I⁻ contacts are 3.733 (4) and 3.848 (4) Å and involve the iodide which resides in a general position (all three iodides have C···I contacts < 4.1 Å).

Introduction

The current interest in structural ferrocene chemistry focuses on a wide variety of derivatives which may have potential applications in (a) charge-transfer chemistry (Moore *et al.*, 1993) (b) supramolecular chemistry (Beer *et al.*, 1991), (c) non-linear optical materials science (Houlton *et al.*, 1993), (d) ceramics (Tang *et al.* 1993) and (e) molecular inclusion and recognition chemistry (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a,b*).

Hydrogen bonds often provide the strongest intermolecular forces between molecules in organic molecular crystals and hence often dictate the preferred packing arrangement. The general principles underlying hydrogen-bond formation are reasonably well understood and the structures of hydrogen-bonded crystals can often be rationalized in terms of preferred combinations of hydrogen-bond donors and acceptors (Etter, 1990; Etter, McDonald & Bernstein, 1990; Etter & Reutzel, 1991).

We are currently studying the molecular structures, hydrogen-bonding and molecular-interaction patterns in the crystal lattices of a variety of ferrocene

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