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1,1′-Bis(trimethylsilyl)ferrocenium Tetrachloroaluminate(1−), 1,1′-Bis(trimethylsilyl)ferrocene and 1,1′-Dimethylferrocene

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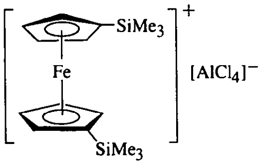
Abstract

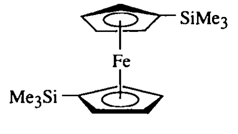
The structures of two substituted ferrocene compounds and one substituted ferrocenium compound have been determined. In compound (1), 1,1′-bis(trimethylsilyl)ferrocenium tetrachloroaluminate(1−), $[Fe\{(CH_3)_3Si\text{-}\eta^5\text{-}C_5H_4\}_2]AlCl_4$, the cyclopentadienyl rings are staggered by 17.7 (2)°. They are also tilted by 4.9 (6)° from parallelism, possibly due to steric interaction between the bulky trimethylsilyl groups, which are intermediate between *cis* and *trans*. The parallel cyclopentadienyl rings in the centrosymmetric molecule of 1,1′-bis(trimethylsilyl)ferrocene, $[Fe\{(CH_3)_3Si\text{-}\eta^5\text{-}C_5H_4\}_2]$, (2), are ideally staggered and the trimethylsilyl groups are *trans* to each other. In 1,1′-dimethylferrocene, $[Fe(CH_3\text{-}\eta^5\text{-}C_5H_4)_2]$, (3), the rings are virtually eclipsed and the methyl groups have a *cis* conformation.

Comment

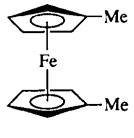
The interest in preparing polymers containing skeletal transition metals is driven by the possibility of unusual and novel electrochemical, magnetic and preceramic properties for these materials (Sheats, Carraher & Pittman, 1985; Manners, 1994). We have recently reported that high molecular weight poly(ferrocenylsilanes) in the presence of an oxidizing agent such as I_2 will convert to a partially oxidized material containing both ferrocene and ferrocenium moieties in the polymer backbone (Foucher, Tang & Manners, 1992; Rulkens, Lough & Manners, 1994; Foucher, Ziembinski, Rulkens, Nelson & Manners, 1994; Lough, Manners & Rulkens, 1994). The syntheses and determination of the structures of 1,1′-bis(trimethylsilyl)ferrocenium tetrachloroaluminate, (1), 1,1′-bis(trimethylsilyl)ferrocene, (2), and 1,1′-dimethylferrocene, (3), were undertaken in order to provide structurally characterized models for oligoferrocenylsilanes and poly(ferrocenylsilanes).



(1)



(2)



(3)

Many structures of ferrocenium salts have been determined to date but a search of the October 1994 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed that (1) was the first to contain an $AlCl_4^-$ anion. Compound (1) crystallizes as two discrete ionic moieties; the shortest carbon-to-chlorine distance between the anion and cation is 3.582 (3) Å for C(3)···Cl(1). In (1), the trimethylsilyl groups are intermediate between *cis* and *trans* with a C(1)···Cp(centroid)···Cp(centroid)···C(6) dihedral angle of 89.1 (2)°, and the cyclopentadienyl rings are staggered by 17.7 (2)° [this angle is defined by the torsion angle C(1)···Cp(centroid)···Cp(centroid)···C(10)]. In (2), however, the Fe atom lies on an inversion center, the trimethylsilyl substituents are fully *trans* and the Cp rings have an ideally staggered conformation. The geometry about the Si atoms in (1) and (2) is virtually tetrahedral, although the smallest tetrahedral angles in (1), C(1)—Si(1)—C(12) [104.8 (2)°] and C(6)—Si(2)—C(16) [106.2 (3)°], indicate some distortion caused by the relatively close proximity of the trimethylsilyl groups.

The distances from the Fe atom to the centroids of the cyclopentadienyl rings in (1) are both 1.705 (6) Å, significantly longer than in (2), where the equivalent distance is 1.656 (2) Å. The Fe—C(ring) distances in both (1) and (2) are longest for the Si-substituted C(ring) atoms; 2.110 (5) Å for Fe—C(1) and 2.115 (5) Å for Fe—C(6) in (1) and 2.0649 (13) Å for Fe(1)—C(1) in (2). In (1), these longer Fe—C(ring) distances result in a tilting of the cyclopentadienyl rings by 4.9 (6)° from parallelism. This tilt probably affords relief from the steric interaction between the bulky trimethylsilyl substituents in this conformation, which is intermediate between *cis* and *trans*. In (2), however, by virtue of crystallographic symmetry, the Cp rings are ideally parallel. The C(ring)—Si distance of 1.888 (5) Å for both Si(1)—C(1) and Si(2)—C(6) in (1) is slightly longer than the Si(1)—C(1) distance of 1.8587 (14) in (2).

Two previously studied structures similar to (1) and (2) are those of 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocene (Okuda & Herdtweck, 1989) and 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)ferrocene (Okuda & Herdtweck, 1988). For these compounds, as with (1) and (2), the orientations of bulky trimethylsilyl substituents also play an important role in controlling the conformation of the molecules. In the structure of 1,1′-dimethylferrocene, (3), the two methyl substituents are in the *cis* conformation and the cyclopentadienyl rings are almost eclipsed with a C(1)···Cp(centroid)···Cp(centroid)···C(6) dihedral angle of 2.6 (3)°. The Fe-to-ring-centroid distances in (3) are 1.650 (6) and 1.649 (6). In the structure of 1,1′-dimethylferrocenium bis(tetracyanoquinodimethane), (4), which was characterized by Wilson *et al.* (1979), the ferrocene moiety lies on a crystallographic inversion center. As a result, the methyl groups are *trans* and the rings are ideally staggered. The conformations of (3) and (4) are in contrast to those of the trimethylsilylferrocenium and ferrocene analogues (1) and (2). The substituent groups in (3) and (4) are not as bulky as the trimethylsilyl groups in (1) and (2) and hence, even though the methyl groups are almost eclipsed in (3), the steric interaction of the these substituents causes only a slight tilting of the rings by 2.4 (2)° from parallelism. The cyclopentadienyl rings in compound (4) are ideally parallel because of crystallographic symmetry.

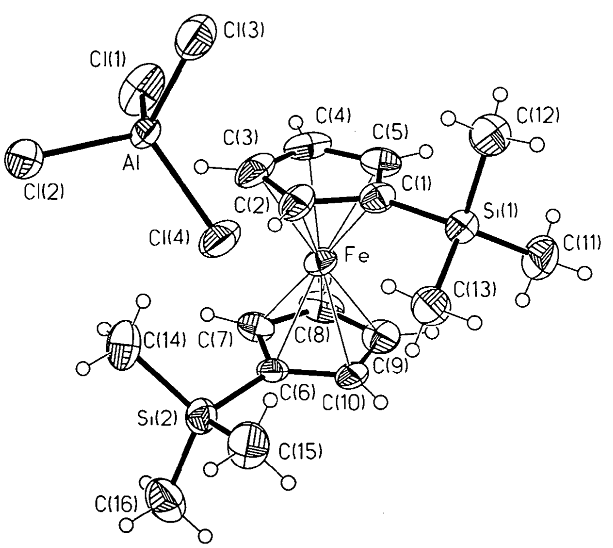


Fig. 1. View of (1) with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% level and H atoms are shown as spheres of arbitrary radii.

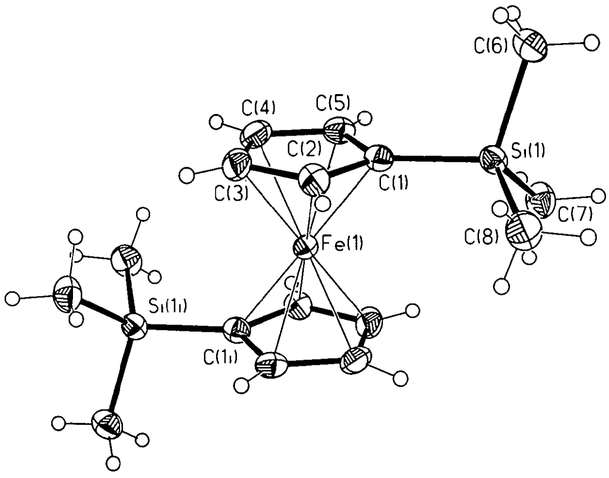


Fig. 2. View of (2) with the crystallographic numbering scheme. The symmetry-related part of the molecule is generated by the operator $-x$, $1-y$, $-z$. Displacement ellipsoids are drawn at the 50% level and H atoms are shown as spheres of arbitrary radii.

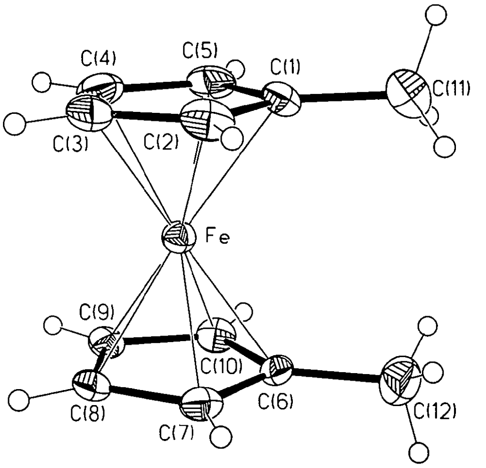


Fig. 3. View of (3) with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% level and H atoms are shown as spheres of arbitrary radii.

Experimental

1,1′-Bis(trimethylsilyl)ferrocene, (2) (which is a liquid at room temperature), was prepared by the method of Rausch, Vogel & Rosenberg (1957). To 5.00 g (15.2 mmol) of (2) in toluene were added 0.40 g (3.00 mmol) of aluminium trichloride and an excess of trimethylchlorosilane (9.8 g, 91 mmol). The red solution was refluxed for three hours and turned dark blue. Filtration, followed by removal of solvent and excess 1,1′-bis(trimethylsilyl)ferrocene led to the isolation of a blue powder. Recrystallization of the powder from freshly distilled tetrahydrofuran led to the formation of dark blue needles of (1) (0.85 g, 1.70 mmol) in a 57% yield based on aluminium trichloride.

Crystals of (2) were grown at 203 K in a low temperature refrigerator. These were then transferred to a slide cooled by solid carbon dioxide. A suitable crystal was mounted in epoxy and transferred into the cold nitrogen stream (173 K) of a low-temperature unit.

1,1′-Dimethylferrocene, (3), is commercially available from Aldrich Chemical Company.

Compound (1)

Crystal data

$[Fe(C_8H_{13}Si)_2][AlCl_4]$
$M_r = 499.2$
Monoclinic
$P2_1/c$
$a = 11.154\ (2)$ Å
$b = 15.059\ (3)$ Å
$c = 14.641\ (3)$ Å
$\beta = 90.37\ (2)^\circ$
$V = 2459.1\ (8)$ Å^3
$Z = 4$
$D_x = 1.348$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.7\text{–}16.5^\circ$
$\mu = 1.180$ mm^{-1}
$T = 173\ (2)$ K
Rectangular block
0.60 × 0.30 × 0.30 mm
Dark blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: *XEMP* in *SHELXTL/PC* (Sheldrick, 1990) using ψ-scan data
$T_{min} = 0.508$, $T_{max} = 0.599$
5482 measured reflections
5197 independent reflections

3050 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0279$
$\theta_{max} = 26.3^\circ$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: 14% (linear correction)

Refinement

Refinement on F
$R = 0.0522$
$wR = 0.0692$
$S = 1.10$
3050 reflections
218 parameters
H atoms treated using a riding model
$w = 1/[\sigma^2(F) + 0.0022F^2]$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe	0.0279 (1)	0.7713 (1)	0.2648 (1)	0.030 (1)
Si(1)	0.0739 (1)	0.8123 (1)	0.0245 (1)	0.036 (1)
Si(2)	0.0238 (1)	0.5337 (1)	0.2957 (1)	0.038 (1)
C(1)	0.1184 (4)	0.8198 (3)	0.1489 (3)	0.032 (2)
C(2)	0.1941 (5)	0.7592 (4)	0.1997 (4)	0.038 (2)
C(3)	0.2111 (5)	0.7923 (4)	0.2897 (4)	0.045 (2)
C(4)	0.1468 (5)	0.8734 (4)	0.2960 (4)	0.048 (2)
C(5)	0.0910 (5)	0.8892 (4)	0.2111 (4)	0.038 (2)
C(6)	−0.0480 (4)	0.6472 (3)	0.2995 (3)	0.030 (2)
C(7)	−0.0459 (5)	0.7068 (3)	0.3759 (4)	0.038 (2)
C(8)	−0.1144 (5)	0.7836 (4)	0.3552 (4)	0.044 (2)
C(9)	−0.1595 (5)	0.7735 (4)	0.2659 (5)	0.045 (2)
C(10)	−0.1185 (4)	0.6899 (4)	0.2320 (4)	0.036 (2)
C(11)	−0.0761 (6)	0.8638 (5)	0.0114 (5)	0.065 (3)
C(12)	0.1891 (5)	0.8786 (4)	−0.0370 (4)	0.048 (2)
C(13)	0.0770 (6)	0.6940 (4)	−0.0109 (4)	0.052 (2)
C(14)	0.1749 (5)	0.5418 (4)	0.3491 (4)	0.055 (2)
C(15)	0.0341 (6)	0.4965 (4)	0.1752 (4)	0.056 (2)
C(16)	−0.0742 (6)	0.4594 (4)	0.3639 (5)	0.061 (3)
Al	0.5547 (1)	0.6280 (1)	0.1389 (1)	0.030 (1)
Cl(1)	0.5105 (2)	0.7172 (1)	0.2474 (1)	0.062 (1)
Cl(2)	0.6549 (1)	0.5194 (1)	0.1937 (1)	0.057 (1)
Cl(3)	0.6622 (1)	0.6972 (1)	0.0415 (1)	0.062 (1)
Cl(4)	0.3916 (1)	0.5838 (1)	0.0759 (1)	0.052 (1)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

Fe—C(1)	2.110 (5)	Fe—C(10)	2.095 (5)
Fe—C(2)	2.098 (5)	Si(1)—C(1)	1.888 (5)
Fe—C(3)	2.097 (5)	Si(1)—C(11)	1.853 (7)
Fe—C(4)	2.080 (6)	Si(1)—C(12)	1.864 (6)
Fe—C(5)	2.067 (6)	Si(1)—C(13)	1.855 (6)
Fe—C(6)	2.115 (5)	Si(2)—C(6)	1.888 (5)
Fe—C(7)	2.070 (6)	Si(2)—C(14)	1.856 (6)
Fe—C(8)	2.081 (6)	Si(2)—C(15)	1.855 (6)
Fe—C(9)	2.091 (5)	Si(2)—C(16)	1.860 (7)
C(1)—Si(1)—C(11)	107.9 (3)	C(14)—Si(2)—C(15)	111.0 (3)
C(1)—Si(1)—C(12)	104.8 (2)	C(6)—Si(2)—C(16)	106.2 (3)
C(11)—Si(1)—C(12)	110.5 (3)	C(14)—Si(2)—C(16)	110.4 (3)
C(1)—Si(1)—C(13)	108.8 (3)	C(15)—Si(2)—C(16)	111.6 (3)
C(11)—Si(1)—C(13)	113.1 (3)	Si(1)—C(1)—C(2)	127.4 (4)
C(12)—Si(1)—C(13)	111.4 (3)	Si(1)—C(1)—C(5)	127.3 (4)
C(6)—Si(2)—C(14)	108.2 (3)	Si(2)—C(6)—C(7)	125.7 (4)
C(6)—Si(2)—C(15)	109.2 (3)	Si(2)—C(6)—C(10)	128.7 (4)

Compound (2)

Crystal data

$[Fe(C_8H_{13}Si)_2]$
$M_r = 330.40$
Monoclinic
$P2_1/c$
$a = 6.173\ (2)$ Å
$b = 8.103\ (1)$ Å
$c = 16.915\ (3)$ Å
$\beta = 95.69\ (2)^\circ$
$V = 841.9\ (3)$ Å^3
$Z = 2$
$D_x = 1.303$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 35 reflections
$\theta = 4.46\text{–}13.24^\circ$
$\mu = 1.024$ mm^{-1}
$T = 173\ (2)$ K
Block
0.56 × 0.46 × 0.44 mm
Pale orange

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: semi-empirical, *SHELXA*90 in *SHELXL*93 (Sheldrick, 1993)
$T_{min} = 0.447$, $T_{max} = 0.927$
2652 measured reflections
2448 independent reflections

2213 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0187$
$\theta_{max} = 29.99°$
$h = -8 \rightarrow 0$
$k = -11 \rightarrow 0$
$l = -23 \rightarrow 23$
3 standard reflections monitored every 97 reflections intensity decay: <5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0279$
$wR(F^2) = 0.0800$
$S = 1.086$
2448 reflections
140 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.1976P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.017$
$\Delta\rho_{max} = 0.366$ e Å^{-3}
$\Delta\rho_{min} = -0.270$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe	0	1/2	0	0.01796 (9)
Si(1)	0.25679 (6)	0.24308 (4)	0.15195 (2)	0.02153 (10)
C(1)	0.1490 (2)	0.4433 (2)	0.11140 (7)	0.0213 (2)
C(2)	−0.0646 (2)	0.5075 (2)	0.11632 (8)	0.0243 (3)
C(3)	−0.0784 (3)	0.6684 (2)	0.08314 (8)	0.0285 (3)
C(4)	0.1266 (3)	0.7069 (2)	0.05679 (8)	0.0295 (3)
C(5)	0.2668 (2)	0.5697 (2)	0.07405 (8)	0.0253 (3)
C(6)	0.4272 (3)	0.2859 (2)	0.24718 (9)	0.0313 (3)
C(7)	0.4272 (3)	0.1421 (2)	0.08097 (9)	0.0322 (3)
C(8)	0.0260 (3)	0.1059 (2)	0.17083 (10)	0.0338 (3)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

Fe—C(1)	2.0649 (13)	Si(1)—C(1)	1.8587 (14)
Fe—C(2)	2.0469 (13)	Si(1)—C(8)	1.859 (2)
Fe—C(3)	2.0516 (13)	Si(1)—C(7)	1.862 (2)
Fe—C(4)	2.0482 (14)	Si(1)—C(6)	1.867 (2)
Fe—C(5)	2.0472 (14)		
C(1)—Si(1)—C(8)	109.44 (7)	C(8)—Si(1)—C(6)	109.79 (8)
C(1)—Si(1)—C(7)	110.49 (7)	C(7)—Si(1)—C(6)	109.39 (8)
C(8)—Si(1)—C(7)	109.84 (8)	C(2)—C(1)—Si(1)	126.56 (10)
C(1)—Si(1)—C(6)	107.86 (7)	C(5)—C(1)—Si(1)	127.26 (10)

Compound (3)

Crystal data

$[Fe(C_6H_7)_2]$
$M_r = 214.1$
Monoclinic
$P2_1/c$
$a = 12.190$ (2) Å
$b = 7.466$ (2) Å
$c = 10.839$ (2) Å
$\beta = 103.25$ (3)°

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.9–18.3°$
$\mu = 1.515$ mm^{-1}
$T = 173$ (2) K
Flat block

$V = 960.2$ (3) Å^3
$Z = 4$
$D_x = 1.481$ Mg m^{-3}

0.42 × 0.35 × 0.13 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: semi-empirical, *SHELXA*90 in *SHELXL*93 (Sheldrick, 1993)
$T_{min} = 0.588$, $T_{max} = 0.893$
1600 measured reflections
1369 independent reflections

1002 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0382$
$\theta_{max} = 23.4°$
$h = -13 \rightarrow 0$
$k = -8 \rightarrow 0$
$l = -11 \rightarrow 11$
3 standard reflections frequency: 120 min intensity decay: <5%

Refinement

Refinement on F
$R = 0.0434$
$wR = 0.0523$
$S = 1.22$
1002 reflections
122 parameters
H atoms treated using a riding model
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Extinction correction: refined, empirical, isotropic (*SHELXTL*/*PC*; Sheldrick, 1990)
Extinction coefficient: 0.0005 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (3)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe	0.29673 (7)	0.01735 (10)	0.09047 (7)	0.0166 (3)
C(1)	0.2380 (5)	0.1307 (7)	0.2364 (5)	0.020 (2)
C(2)	0.2407 (5)	0.2574 (7)	0.1415 (6)	0.026 (2)
C(3)	0.3525 (6)	0.2730 (8)	0.1263 (6)	0.028 (2)
C(4)	0.4196 (6)	0.1540 (8)	0.2120 (6)	0.031 (2)
C(5)	0.3501 (5)	0.0657 (8)	0.2800 (5)	0.028 (2)
C(6)	0.1914 (5)	−0.1882 (7)	0.0144 (5)	0.018 (2)
C(7)	0.1991 (5)	−0.0611 (7)	−0.0807 (5)	0.022 (2)
C(8)	0.3132 (5)	−0.0488 (7)	−0.0872 (5)	0.021 (2)
C(9)	0.3779 (5)	−0.1669 (7)	0.0043 (5)	0.021 (2)
C(10)	0.3003 (5)	−0.2533 (7)	0.0663 (5)	0.022 (2)
C(11)	0.1386 (6)	0.0767 (9)	0.2863 (6)	0.037 (2)
C(12)	0.0846 (6)	−0.2493 (9)	0.0481 (6)	0.036 (2)

Table 6. *Selected geometric parameters* (Å, °) *for* (3)

Fe—C(1)	2.062 (6)	Fe—C(7)	2.047 (5)
Fe—C(2)	2.040 (6)	Fe—C(8)	2.042 (6)
Fe—C(3)	2.034 (6)	Fe—C(9)	2.041 (6)
Fe—C(4)	2.029 (6)	Fe—C(10)	2.039 (5)
Fe—C(5)	2.040 (5)	C(1)—C(11)	1.491 (10)
Fe—C(6)	2.049 (5)	C(6)—C(12)	1.501 (9)
Fe—C(1)—C(11)	128.4 (4)	Fe—C(6)—C(12)	128.9 (4)
C(2)—C(1)—C(11)	127.3 (5)	C(7)—C(6)—C(12)	125.8 (5)
C(5)—C(1)—C(11)	125.8 (5)	C(10)—C(6)—C(12)	126.1 (5)

The refined C—H distances for compound (2) range from 0.88 (2) to 1.01 (2) Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989) for (1) and (3); *XSCANS* (Siemens, 1994) for (2). Cell refinement: *CAD*-4 *Software* for (1) and (3); *XSCANS* for (2). Data reduction: *XCAD*4 (Siemens, 1993) for (1) and (3); *XSCANS* for (2). For all compounds, program(s) used to solve structures: *XS* in *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structures: *XLS*3 in *SHELXTL/PC* for (1) and (3); *SHELXL*93 (Sheldrick, 1993) for (2). For all compounds, molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *XPUBL* in *SHELXTL/PC* for (1) and (3); *SHELXL*93 for (2).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms for (1) and (3), and complete geometry for (2) have been deposited with the IUCr (Reference: FG1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Strongly Luminescent Organic-Solvent-Soluble Salt of the Tris(dipicolinato)-europium(III) Trianion

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Abstract

The tetraethylammonium salt of the $[Eu(dipic)_3]^{3-}$ (dipic = 2,6-pyridinedicarboxylate) complex anion, tris(tetraethylammonium) tris(2,6-pyridinedicarboxylato-*N*,*O*,*O*″)europium(III) tetrahydrate, $(C_8H_{20}N)_3[Eu(C_7H_3NO_4)_3].4H_2O$, forms monoclinic crystals. The lattice contains alternating columns of the Δ and Λ enantiomeric forms of the trianion, with the water molecules hydrogen bonded to the uncoordinated O atoms of the carboxylate groups and the tetraethylammonium cations forming columns, presumably to optimize electrostatic attractions.

Comment

Luminescence of rare earth cations such as Eu^{III} and Tb^{III} is enhanced by the exclusion of water from the metal coordination sphere and by the binding of rigid ligands (Bünzli & Choppin, 1989). Tris(dipicolinato) [dipicolinate (dipic) = pyridine-2,6-dicarboxylate] complexes of rare earth metals, in which the metal is bound with D_3 nine-coordinate stereochemistry to six O- and three N-donor atoms of the ligands, are well known as strong emitters in solution (Riehl & Richardson, 1986; Dong & Flint, 1992). Enantioselective quenching of this emission by chiral transition metal–polyamine complexes in solution has been demonstrated (Metcalf, Bolender, Driver & Richardson, 1993) and we have shown recently that the emission is almost totally quenched in solid salts formed from rare earth complex anions and such cations (Brayshaw, Bünzli, Froidevaux, Harrowfield, Kim & Sobolev, 1995). Structural studies reveal extensive hydrogen-bonding interactions between the NH groups of the cations and the carboxylate O atoms of the anions in these salts (Harrowfield, Kim,

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