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Organic Metal $(DIMET)_2BF_4$

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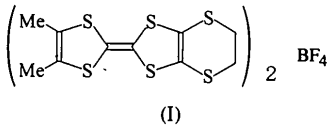
Abstract

The crystal structure of bis[2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin]ylium tetrafluoroborate, $2(C_{10}H_{10}S_6^{0.5+}).BF_4^-$, is constructed of two types of column which consist of donor molecules stacked along two crystallographic axes.

Comment

The donor molecule DIMET [dimethyl(ethylenedithio)-tetrathiafulvalene] is an all-sulfur analogue of DMET [dimethyl(ethylenedithio)diselenadithiafulvalene]. Recently, organic conducting salts, including the title compound, (I), were investigated for their electrical properties (Yoshino, Saito, Kikuchi & Ikemoto, 1995). These radical salts consist of unsymmetrical donors, having a DMET-type framework, and small tetrahedral anions. In order to compare these structures, the crystal structure analysis of the title compound was performed.



(I)

The result of the structure analysis shows that $(DIMET)_2BF_4$ is isostructural with $(DMET)_2BF_4$ (Ishikawa, Saito, Kikuchi, Kobayashi & Ikemoto, 1991), $(DMET)_2ClO_4$ (Takhirov *et al.*, 1989) and $(DIMET)_2ClO_4$ (Endres, Heid, Keller, Heinen & Schweitzer, 1987; Takhirov *et al.*, 1990). There are two independent molecules which form columns in the assymetric unit. The ethylenedithio moiety (—S—CH_2—CH_2—S—) of the DIMET molecule *A* shows disorder at C10*A*. The *A* molecules stack along the *a* axis (column *A*). The molecular plane of DIMET in column *A* was calculated for S1*A*, S2*A*, S5*A*, S6*A*, C1*A* and C2*A*. In column *A*, the interplanar distances between two neighbouring molecules related by the inversion centres (0, 0, 0) and (1/2, 0, 0) are the same [3.49 Å] within experimental error.

In column *B*, the interplanar distances between two neighbouring molecules related by the inversion centres (0, 1/2, 1/2) and (0, 0, 1/2) are 3.59 and 3.48 Å, respectively. This shows a rather stronger dimerization of donor molecules than in other good organic columnar conductors, such as the DMET salts (Ishikawa, Kikuchi, Saito, Ikemoto & Kobayashi, 1989; Ishikawa, Saito, Kikuchi, Kobayashi & Ikemoto, 1991).

Only a few intra- and intercolumnar contacts exist that are shorter than the sum of the van der Waals radii; these are between the S atoms of the *A* molecules in the *A* columns. No short S—S contacts exist between the *B* molecules of the *B* columns.

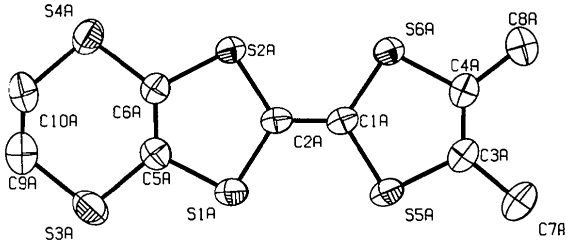


Fig. 1. Displacement ellipsoid plot (50% probability) of molecule *A* of the title compound showing the atom-labelling scheme.

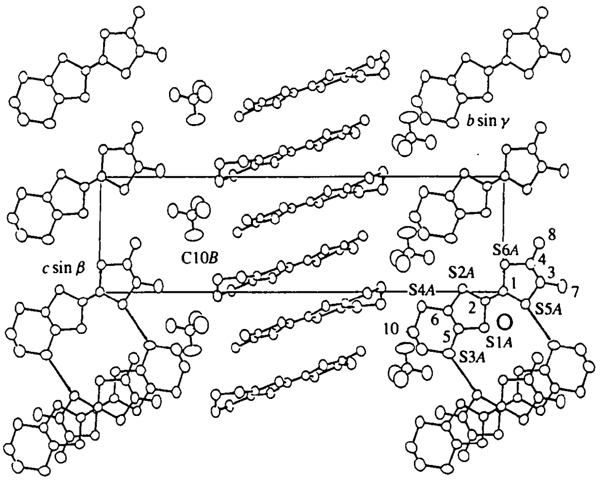


Fig. 2. Crystal structure of $(DIMET)_2BF_4$ viewed alng the *a* axis. Displacement ellipsoids indicate the region of 50% probability. Thin solid lines show the intermolecular contacts shorter than the sum of van der Waals radii.

Experimental

Crystals of $(DIMET)_2BF_4$ were prepared by electrochemical oxidation of DIMET in 1,1,2-trichloroethane solution in the presence of $(^nBu_4N)BF_4$ and at constant current (1 μA).

Crystal data

$2(C_{10}H_{10}S_6^{0.5+}).BF_4^-$
$M_r = 731.89$

Mo *K*α radiation
$\lambda = 0.71068$ Å

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Triclinic
$P\bar{1}$
$a = 6.999\ (1)$ Å
$b = 7.787\ (2)$ Å
$c = 26.933\ (3)$ Å
$\alpha = 91.68\ (2)°$
$\beta = 89.54\ (1)°$
$\gamma = 105.37\ (2)°$
$V = 1414.8\ (5)$ Å^3
$Z = 2$
$D_x = 1.718$ Mg m^{-3}

Cell parameters from 20 reflections
$\theta = 14.5–15.5°$
$\mu = 0.9304$ mm^{-1}
$T = 293$ K
Plate
0.63 × 0.63 × 0.13 mm
Black

Data collection

Rigaku AFC-*M* diffractometer
2θ–ω scans
Absorption correction: Gaussian integration (*UNICS*III; Sakurai & Kobayashi, 1979)
$T_{\min} = 0.564$, $T_{\max} = 0.889$
6828 measured reflections
6486 independent reflections

5695 observed reflections $[F > 3\sigma(F)]$
$R_{\text{int}} = 0.0256$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 34$
3 standard reflections monitored every 100 reflections intensity decay: 1.8%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.043$
$S = 4.38$
5695 reflections
399 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.00001F^2]$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.03$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
S1*A*	0.1772 (1)	−0.3127 (1)	0.04334 (3)	0.0421 (3)
S2*A*	0.2811 (1)	0.0276 (1)	0.09943 (3)	0.0381 (3)
S3*A*	0.1242 (1)	−0.5392 (1)	0.13003 (4)	0.0594 (4)
S4*A*	0.2471 (1)	−0.1325 (1)	0.19824 (3)	0.0519 (3)
S5*A*	0.2117 (1)	−0.1053 (1)	−0.05869 (3)	0.0434 (3)
S6*A*	0.3076 (1)	0.2359 (1)	−0.00457 (3)	0.0408 (3)
C1*A*	0.2508 (4)	0.0063 (4)	−0.0017 (1)	0.036 (1)
C2*A*	0.2370 (4)	−0.0811 (4)	0.0418 (1)	0.035 (1)
C3*A*	0.2535 (4)	0.0852 (4)	−0.0940 (1)	0.041 (1)
C4*A*	0.2976 (4)	0.2414 (4)	−0.0693 (1)	0.041 (1)
C5*A*	0.1826 (4)	−0.3225 (4)	0.1079 (1)	0.042 (1)
C6*A*	0.2290 (4)	−0.1665 (4)	0.1337 (1)	0.038 (1)
C7*A*	0.2353 (5)	0.0511 (5)	−0.1491 (1)	0.056 (1)
C8*A*	0.3435 (5)	0.4251 (5)	−0.0900 (1)	0.055 (1)
C9*A*	0.1225 (8)	−0.5014 (6)	0.1966 (2)	0.100 (2)
C10*A*	0.2265 (12)	−0.3518 (6)	0.2183 (2)	0.175 (4)
S1*B*	−0.1711 (1)	0.1223 (1)	0.56600 (3)	0.0402 (3)
S2*B*	0.2559 (1)	0.2211 (1)	0.54485 (3)	0.0424 (3)
S3*B*	−0.1375 (1)	0.0127 (1)	0.66804 (3)	0.0470 (3)
S4*B*	0.3763 (1)	0.1294 (1)	0.64278 (3)	0.0519 (3)
S5*B*	−0.2544 (1)	0.2651 (1)	0.45882 (3)	0.0413 (3)
S6*B*	0.1699 (1)	0.3642 (1)	0.43793 (3)	0.0421 (3)
C1*B*	−0.0175 (4)	0.2733 (4)	0.4795 (1)	0.036 (1)
C2*B*	0.0187 (4)	0.2129 (4)	0.5246 (1)	0.036 (1)
C3*B*	−0.1806 (4)	0.3567 (4)	0.4012 (1)	0.037 (1)
C4*B*	0.0140 (4)	0.4018 (4)	0.3914 (1)	0.037 (1)
C5*B*	−0.0130 (4)	0.0979 (4)	0.6140 (1)	0.036 (1)
C6*B*	0.1825 (4)	0.1420 (4)	0.6039 (1)	0.037 (1)
C7*B*	−0.3447 (5)	0.3749 (4)	0.3682 (1)	0.052 (1)
C8*B*	0.1142 (5)	0.4837 (4)	0.3453 (1)	0.050 (1)
C9*B*	0.0611 (5)	−0.0350 (5)	0.7028 (1)	0.052 (1)
C10*B*	0.2504 (5)	0.1089 (4)	0.7026 (1)	0.055 (1)
B	0.5645 (6)	0.3302 (5)	0.2310 (2)	0.054 (2)
F1	0.6469 (4)	0.5084 (3)	0.2369 (1)	0.105 (1)
F2	0.6922 (4)	0.2387 (4)	0.2454 (1)	0.108 (1)
F3	0.3952 (4)	0.2849 (4)	0.2584 (1)	0.108 (1)
F4	0.5207 (4)	0.2917 (3)	0.1822 (1)	0.094 (1)

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

S1*A*—C2*A*	1.741 (3)	S1*B*—C2*B*	1.741 (3)
S1*A*—C5*A*	1.743 (3)	S1*B*—C5*B*	1.755 (3)
S2*A*—C2*A*	1.736 (3)	S2*B*—C2*B*	1.737 (3)
S2*A*—C6*A*	1.746 (3)	S2*B*—C6*B*	1.747 (3)
S3*A*—C5*A*	1.749 (3)	S3*B*—C5*B*	1.746 (3)
S3*A*—C9*A*	1.809 (4)	S3*B*—C9*B*	1.807 (4)
S4*A*—C6*A*	1.752 (3)	S4*B*—C6*B*	1.744 (3)
S4*A*—C10*A*	1.775 (5)	S4*B*—C10*B*	1.821 (4)
S5*A*—C1*A*	1.728 (3)	S5*B*—C1*B*	1.738 (3)
S5*A*—C3*A*	1.743 (3)	S5*B*—C3*B*	1.743 (3)
S6*A*—C1*A*	1.730 (3)	S6*B*—C1*B*	1.733 (3)
S6*A*—C4*A*	1.747 (3)	S6*B*—C4*B*	1.748 (3)
C1*A*—C2*A*	1.363 (4)	C1*B*—C2*B*	1.364 (4)
C3*A*—C4*A*	1.332 (4)	C3*B*—C4*B*	1.339 (4)
C3*A*—C7*A*	1.501 (4)	C3*B*—C7*B*	1.497 (5)
C4*A*—C8*A*	1.504 (5)	C4*B*—C8*B*	1.496 (4)
C5*A*—C6*A*	1.345 (4)	C5*B*—C6*B*	1.347 (4)
B—F1	1.359 (4)	C9*B*—C10*B*	1.491 (4)
B—F2	1.348 (6)	B—F3	1.361 (5)
C9*A*—C10*A*	1.321 (6)	B—F4	1.359 (5)
C2*A*—S1*A*—C5*A*	95.5 (1)	C2*B*—S1*B*—C5*B*	95.2 (1)
C2*A*—S2*A*—C6*A*	95.5 (1)	C2*B*—S2*B*—C6*B*	95.3 (1)
C5*A*—S3*A*—C9*A*	102.5 (2)	C5*B*—S3*B*—C9*B*	101.0 (2)
C6*A*—S4*A*—C10*A*	101.4 (2)	C6*B*—S4*B*—C10*B*	100.2 (2)
C1*A*—S5*A*—C3*A*	95.8 (1)	C1*B*—S5*B*—C3*B*	95.9 (1)
C1*A*—S6*A*—C4*A*	95.6 (1)	C1*B*—S6*B*—C4*B*	95.9 (1)
S5*A*—C1*A*—S6*A*	114.8 (2)	S5*B*—C1*B*—S6*B*	114.4 (2)
S5*A*—C1*A*—C2*A*	122.2 (2)	S5*B*—C1*B*—C2*B*	123.0 (2)
S6*A*—C1*A*—C2*A*	123.1 (2)	S6*B*—C1*B*—C2*B*	122.6 (2)
S1*A*—C2*A*—S2*A*	114.9 (2)	S1*B*—C2*B*—S2*B*	115.2 (2)
S1*A*—C2*A*—C1*A*	121.9 (2)	S1*B*—C2*B*—C1*B*	122.1 (2)
S2*A*—C2*A*—C1*A*	123.2 (2)	S2*B*—C2*B*—C1*B*	122.7 (2)
S5*A*—C3*A*—C4*A*	116.9 (2)	S5*B*—C3*B*—C4*B*	117.0 (2)
S5*A*—C3*A*—C7*A*	115.0 (2)	S5*B*—C3*B*—C7*B*	115.4 (2)
C4*A*—C3*A*—C7*A*	128.1 (3)	C4*B*—C3*B*—C7*B*	127.6 (3)
S6*A*—C4*A*—C3*A*	116.9 (2)	S6*B*—C4*B*—C3*B*	116.8 (2)
S6*A*—C4*A*—C8*A*	114.9 (2)	S6*B*—C4*B*—C8*B*	116.0 (2)
C3*A*—C4*A*—C8*A*	128.2 (3)	C3*B*—C4*B*—C8*B*	127.2 (3)
S1*A*—C5*A*—S3*A*	114.0 (2)	S1*B*—C5*B*—S3*B*	113.7 (2)
S1*A*—C5*A*—C6*A*	117.0 (2)	S1*B*—C5*B*—C6*B*	116.8 (2)
S3*A*—C5*A*—C6*A*	128.9 (3)	S3*B*—C5*B*—C6*B*	129.5 (2)
S2*A*—C6*A*—S4*A*	115.1 (2)	S2*B*—C6*B*—S4*B*	114.7 (2)
S2*A*—C6*A*—C5*A*	117.1 (2)	S2*B*—C6*B*—C5*B*	117.3 (2)
S4*A*—C6*A*—C5*A*	127.8 (2)	S4*B*—C6*B*—C5*B*	128.1 (2)
S3*A*—C9*A*—C10*A*	122.1 (4)	S3*B*—C9*B*—C10*B*	114.5 (3)
S4*A*—C10*A*—C9*A*	126.4 (5)	S4*B*—C10*B*—C9*B*	113.3 (2)
F1—B—F2	110.5 (3)	F2—B—F3	110.4 (3)
F1—B—F3	108.7 (4)	F2—B—F4	108.9 (4)
F1—B—F4	108.7 (3)	F3—B—F4	109.6 (3)

In the least-squares refinement, H atoms were located on the basis of the difference Fourier synthesis, except for those bonded to C9*A* and C10*A*. No correction was made for secondary extinction.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *UNICS*III (Sakurai & Kobayashi, 1979). Molecular graphics: *ORTEP*II (Johnson, 1971).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: OH1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Endres, H., Heid, R., Keller, H. J., Heinen, I. & Schweitzer, D. (1987). *Acta Cryst.* **C43**, 115–117.

Ishikawa, Y., Kikuchi, K., Saito, K., Ikemoto, I. & Kobayashi, K. (1989). *Acta Cryst.* **C45**, 572–575.

Ishikawa, Y., Saito, K., Kikuchi, K., Kobayashi, K. & Ikemoto, I. (1991). *Bull. Chem. Soc. Jpn*, **64**, 212–215.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Sakurai, T. & Kobayashi, K. (1979). *Rep. Inst. Phys. Chem. Res. (Jpn)*, **55**, 69–77.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Takhirov, T. G., Krasochka, O. N., D'yachenko, O. A., Atovmyan, L. O., Aldoshina, M. Z., Gol'denberg, L. M., Lyubovskaya, R. N., Merzhanov, V. A. & Lyubovskii, R. B. (1990). *Sov. J. Chem. Phys.* **7**, 209–221.

Takhirov, T. G., Krasochka, O. N., D'yachenko, O. A., Atovmyan, L. O., Petrov, M. L., Pubtsova, I. K. & Lyubovskaya, R. N. (1989). *Zh. Strukt. Khim.* **30**, 114–121.

Yoshino, H., Saito, K., Kikuchi, K. & Ikemoto, I. (1995). *Synth. Met.* **72**, 141–146.

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Dimethyl 2-Methylcubane-1,4-dicarboxylate and Dimethyl 2,3-Dimethylcubane-1,4-dicarboxylate

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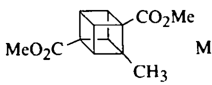
Abstract

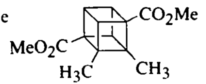
The title compounds, dimethyl 2-methylcubane-1,4-dicarboxylate, $C_{13}H_{14}O_4$, and dimethyl 2,3-dimethylcubane-1,4-dicarboxylate, $C_{14}H_{16}O_4$, are rare examples of alkyl-substituted cubanes. The 1,2-disubstituted cubane C—C bond lengths of both compounds are generally found to be longer than the other cubane C—C bonds. Both compounds show differences in the cubane C—C distances, as well as differences in the conformations of the methyl carboxylate groups.

Comment

The renaissance in cubane chemistry in recent years is in large part due to the discovery (Eaton & Castaldi, 1985) that amide-directed *ortho*-metallation methodology (Snieckus, 1990) could be employed to extend both the range and pattern of substitution of available cubanes (Eaton, Xiong & Gillardi, 1993). This approach, however, is not suitable for the introduction of alkyl groups onto the cubane nucleus. Herein, we report the structures of the title compounds, dimethyl 2-methylcubane-1,4-dicarboxylate, (1) (Lowe, Moorhouse, Walter & Tsanaktsidis, 1994), and dimethyl 2,3-dimethylcubane-1,4-dicarboxylate, (2) (Cristiano & Tsanaktsidis, 1994).



(1)



(2)

The centre of the cubane cage of the monomethyl derivative (1) lies on a centre of symmetry, which results in the methyl substitutent being disordered over two symmetry-related positions. The observed C—CH_3 bond length of 1.384 (6) Å is much shorter than the corresponding value of 1.494 (2) Å found in (2), and is presumably a consequence of this disorder. All other bond lengths are comparable to those found in other cubanes. The cubane C—C distances for (1) (1.550–1.574 Å) are generally found to be slightly shorter than the corresponding values found for (2) (1.553–1.581 Å). In addition, there are significant differences in the conformations of the methyl carboxylate groups, with the torsion angle C(2)—C(1)—C(9)—O(2*A*) being 92 (3)° for (1) and the corresponding value for (2) being −119.4 (2)°. For both compounds, the 1,2-disubstituted C—C distances involving the methyl carboxylate and the methyl groups, 1.574 (2) for (1) and 1.581 (2) Å for (2), are significantly longer than the other cubane C—C distances, while the bond involving the two methyl substitutents in (2) is somewhat shorter, being

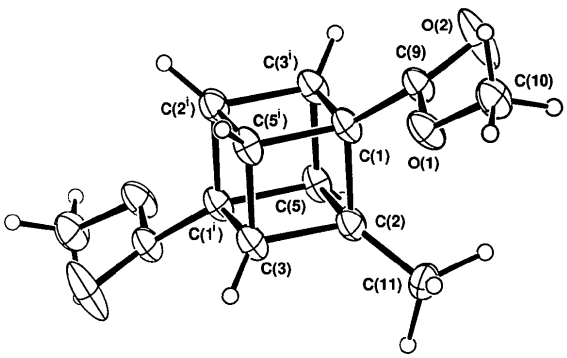


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1). Displacement ellipsoids are drawn at the 50% probability level. Symmetry transformation to generate equivalent atoms: (i) $-x$, $-y$, $-z$.