C11—P1—S1	114.69 (16)	C4—C3—C2	114.4 (4)
C2—C1—P1	111.9 (3)	C31—C3—C2	120.9 (5)
C2—C1—Br1	127.6 (4)	C3—C4—P1	111.0 (3)

The data were collected on a Stoe Imaging Plate Diffraction System (IPDS) [equipped with an Oxford Cryosystems Cryostream cooler device (Cosier & Glazer, 1986) in the cases of (2) and (4)]. For (2), the crystal-to-detector distance was 60 mm. For (3) and (4), the crystal-to-detector distance was chosen to be 80 mm, thus resulting in a θ limitation at 24.27°. For (2) and (3), 125 exposures were obtained with $0 < \varphi < 250°$ and with the crystal rotated through 2° in φ. For (4), 80 exposures were obtained with $0 < \varphi < 200°$ and with the crystals rotated through 2.5° in φ. Coverage of the unique set was over 99% complete to at least 28° for (2), over 96% complete to at least 24° for (3), and over 94% complete to at least 24° for (4). Crystal decay was monitored by measuring 200 reflections per image.

For all compounds, data collection: *IPDS Manual* (Stoe & Cie, 1996*a*); cell refinement: *IPDS Manual*; data reduction: *X-RED* (Stoe & Cie, 1996*b*); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993) for (2) and (3); *SHELXL*97 (Sheldrick, 1997) for (4). For all compounds, molecular graphics: *CAMERON* (Watkin *et al.*, 1996). Software used to prepare material for publication: *SHELXL*93 for (2) and (3); *SHELXL*97 for (4).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1134). Services for accessing these data are described at the back of the journal.

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1,2-Bis(5-methyl-4-methylthio-1,3-dithiolium-2-ylidene)-1,2-diphenylethane Bis(triiodide) and 1,2-Bis(4-methoxyphenyl)-1,2-bis(5-methyl-4-methylthio-1,3-dithiolium-2-ylidene)ethane Diperchlorate

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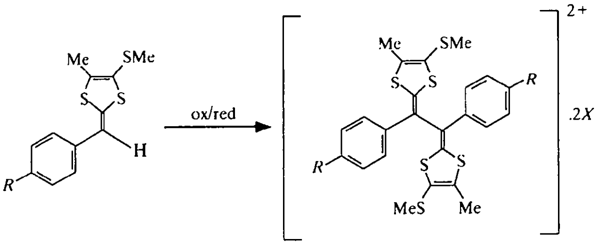
Abstract

The non-planar organic donor 1,2-diaryl-1,2-bis(5-methyl-4-methylthio-1,3-dithiol-2-ylidene)ethane forms dication charge-transfer salts with iodine, $C_{24}H_{22}S_6^{2+}.2I_3^-$, and with perchlorate, $C_{26}H_{26}O_2S_6^{2+}.2ClO_4^-$. In the former salt, mixed stacks of triiodide and dications are observed, while separated organic and inorganic columns are found in the perchlorate salt.

Comment

Extended tetrathiafulvalenes (TTF) which possess a conjugated spacer group between the two dithiole rings have stimulated a lot of work in the field of organic conductors (for a review, see Ogura *et al.*, 1992). The TTF vinylogue derivatives (1*a*) and (1*b*) were prepared by electrochemical synthesis starting from 1,4-dithiafulvene (2) (Lorcy *et al.*, 1995).



(2)

(1*a*) $R = H, X = I_3$
(1*b*) $R = MeO, X = ClO_4$

The stoichiometries of the title charge-transfer salts were determined by X-ray structure analysis: in both cases, there is one donor dication for two anions. Figs. 1 and 2 show the molecular structures of the title compounds. In both of these, the lengths of the

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C═C bonds and the inner S—C bonds (Tables 1 and 2), which are indicative of the charge of the molecules, are close to those observed in similar dicationic extended TTF units (Triki *et al.*, 1993). The crystal structure of (1*a*) is composed of mixed stacks of cations and anions, with the I_3^- counter-ion located between two dithiole moieties. In the case of perchlorate salt (1*b*), the dications stack along the *b* axis. The interplanar separation between successive extended TTF cores is 10.43 (3) Å, too large for there to be any orbital overlap. In both compounds, the phenyl groups are located in a plane perpendicular to that through the dithiole rings; the angles between the planes are 91.5 (2) and 78.7 (1)° for (1*a*) and (1*b*), respectively.

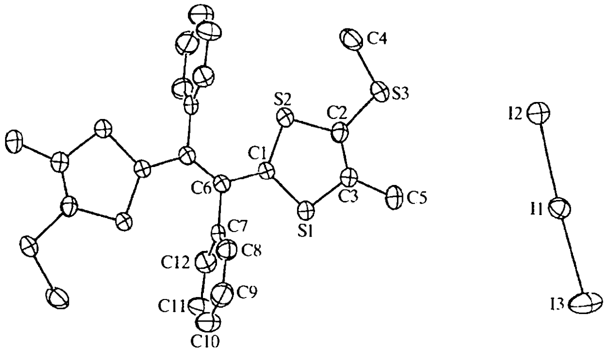

Fig. 1. *ORTEP* drawing of (1*a*) showing 50% probability displacement ellipsoids.

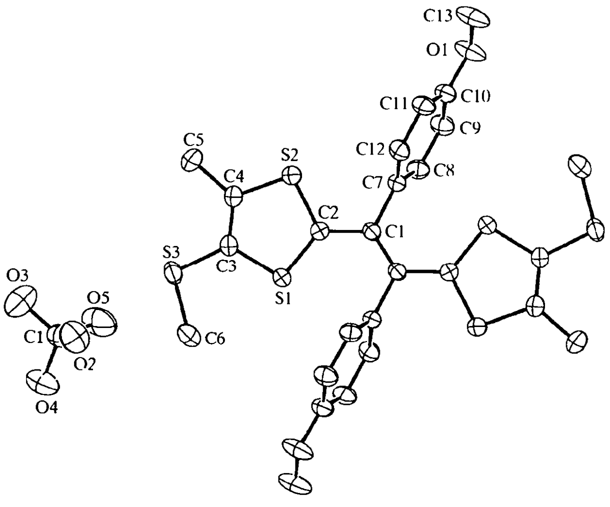

Fig. 2. *ORTEP* drawing of (1*b*) showing 50% probability displacement ellipsoids.

Experimental

The title compounds were obtained by redox chemical reactions. In the case of (1*a*), a CH_2Cl_2 solution was exposed to an iodine atmosphere for a couple of days, while compound (1*b*) was obtained by mixing a tetrahydrofuran solution of the compound with a solution of $Cu(ClO_4)_2.6H_2O$.

Compound (1*a*)

Crystal data

$C_{24}H_{22}S_6^{2+}.2I_3$
$M_r = 1264.18$
Triclinic
$P\bar{1}$
$a = 7.655\,(2)$ Å
$b = 10.867\,(2)$ Å
$c = 12.082\,(2)$ Å
$\alpha = 103.44\,(2)°$
$\beta = 102.75\,(2)°$
$\gamma = 105.89\,(2)°$
$V = 895.6\,(3)$ Å^3
$Z = 1$
$D_x = 2.344$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14$–$24°$
$\mu = 5.567$ mm^{-1}
$T = 293\,(2)$ K
Parallelepiped
0.300 × 0.050 × 0.025 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)
$T_{\min} = 0.686$, $T_{\max} = 0.870$
3800 measured reflections
3521 independent reflections

2105 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 25.97°$
$h = 0 \rightarrow 9$
$k = -13 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.101$
$S = 1.006$
3520 reflections
166 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.013$

$\Delta\rho_{\max} = 0.997$ e Å^{-3}
$\Delta\rho_{\min} = -1.140$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0005 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

I1—I2	2.8904 (9)	S3—C2	1.737 (6)
I1—I3	2.9380 (9)	S3—C4	1.801 (8)
S1—C1	1.679 (6)	C1—C6	1.462 (8)
S1—C3	1.690 (6)	C2—C3	1.364 (9)
S2—C1	1.703 (6)	C3—C5	1.500 (9)
S2—C2	1.722 (6)		
I2—I1—I3	177.40 (3)	C3—C2—S2	116.0 (5)
C1—S1—C3	98.2 (3)	C3—C2—S3	122.4 (5)
C1—S2—C2	96.1 (3)	S2—C2—S3	121.6 (4)
C2—S3—C4	102.9 (3)	C2—C3—C5	125.2 (6)
C6—C1—S1	118.4 (4)	C2—C3—S1	115.3 (5)
C6—C1—S2	127.1 (5)	C5—C3—S1	119.4 (5)
S1—C1—S2	114.4 (3)		

Compound (1*b*)

Crystal data

$C_{26}H_{26}O_2S_6^{2+}.2ClO_4^-$
$M_r = 761.73$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/n$
$a = 11.087$ (5) Å
$b = 10.4329$ (10) Å
$c = 14.325$ (9) Å
$\beta = 104.32$ (2)°
$V = 1605.4$ (13) Å^3
$Z = 2$
$D_x = 1.576$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 14$–22°
$\mu = 0.646$ mm^{-1}
$T = 293$ (2) K
Parallelepiped
0.6 × 0.4 × 0.1 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)
$T_{\min} = 0.822$, $T_{\max} = 0.937$
4029 measured reflections
3840 independent reflections

2751 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 27.91°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 13$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.110$
$S = 1.019$
3840 reflections
203 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.032$

$\Delta\rho_{\max} = 0.486$ e Å^{-3}
$\Delta\rho_{\min} = -0.288$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0022 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1- C2	1.689 (2)	S3—C6	1.788 (3)
S1—C3	1.714 (2)	C1—C2	1.447 (3)
S2—C2	1.695 (2)	C1—C7	1.496 (3)
S2—C4	1.696 (3)	C3—C4	1.366 (3)
S3—C3	1.735 (2)	C4—C5	1.497 (3)
C2—S1—C3	96.50 (12)	C4—C3—S1	116.4 (2)
C2—S2—C4	97.66 (12)	C4—C3—S3	122.3 (2)
C3—S3—C6	101.94 (13)	S1—C3—S3	121.30 (14)
C2—C1—C7	115.2 (2)	C3—C4—C5	125.1 (2)
C1—C2—S1	127.9 (2)	C3—C4—S2	115.0 (2)
C1—C2—S2	117.6 (2)	C5—C4—S2	119.9 (2)
S1—C2—S2	114.40 (14)		

In (1*a*), the highest and deepest residual Fourier difference peaks were located 0.93 Å from I1.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *SHELXL*93.

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2-Amino-3,5-dichloropyridinium Chloride Monohydrate

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Abstract

The monohydrate hydrochloride salt of 2-amino-3,5-dichloropyridine, $C_5H_5Cl_2N_2^+.Cl^-.H_2O$, was isolated from water by slow evaporation. The complex exhibits hydrogen bonds between the halide ions and both the pyridinium [3.109 (2) Å] and amino [3.303 (2) Å] protons. Bond lengths and angles are comparable to those of previously studied pyridine complexes. The C—Cl bond lengths are 1.732 (2) and 1.721 (2) Å, and the C—NH$_2$ bond length is 1.328 (2) Å.

Comment

Our interest in low-dimensional magnetic lattices has resulted in the synthesis and study of a family of compounds with the formula $(LH)_2MX_4$, where M is a transition metal in the 2+ state, X is a halide, Cl or Br, and LH is a protonated organic base. These compounds may pack in a crystal lattice in such a way that low-dimensional magnetic lattices are obtained. The magnetic lattice arises from interactions between the MX_4^{2-} ions. The nature of these interactions is controlled by the crystal lattice, which changes as the organic base is changed. Compounds containing a base with a substituent in the 5 position, such