

A new tetrathiafulvalene–diamide cation salt with $[\text{Cu}_2\text{Br}_4]^{2-}$ anions

Wen Lu, Qin-Yu Zhu, Yong Zhang, Xiao-Min Lin and Jie Dai*

Department of Chemistry, Suzhou University, Suzhou 215123, People's Republic of China

Correspondence e-mail: daijie@suda.edu.cn

Received 20 August 2007

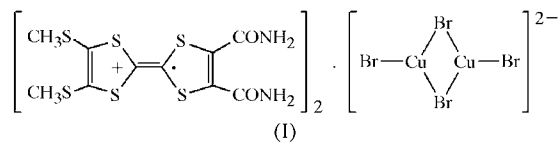
Accepted 27 August 2007

Online 13 October 2007

The title salt, bis[2,3-bis(aminocarbonyl)-8,9-bis(methylsulfanyl)tetrathiafulvalenium] di- μ -bromido-bis[bromido-copper(II)], $(\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2\text{S}_6)_2[\text{Cu}_2\text{Br}_4]$, contains 2,3-bis(aminocarbonyl)-8,9-bis(methylsulfanyl)tetrathiafulvalenium radical cations, $[\text{DMT-TTF}(\text{CONH}_2)_2]^+$, and $[\text{Cu}_2\text{Br}_4]^{2-}$ anions. The cations are associated across centres of inversion in a head-to-tail fashion *via* short face-to-face S \cdots S stacking (TTF moiety). These dimers are further assembled into a one-dimensional chain structure *via* interdimer double S \cdots S contacts involving the methylsulfanyl groups. The one-dimensional chains give rise to a two-dimensional structure through intermolecular double N–H \cdots O hydrogen bonds involving the amide group. The $[\text{Cu}_2\text{Br}_4]^{2-}$ anions, which straddle centres of inversion, are located between the cation layers. Electron paramagnetic resonance measurements show a radical signal, indicating that the two $\text{TTF}^{+\cdot}$ radicals are not completely coupled in the dimer.

Comment

Although tetrathiafulvalene (TTF) and its derivatives have been intensively investigated for several decades, these unique functional molecules continue to attract great attention, especially for their inter- or intramolecular interactions. These weak interactions play a very important role in supramolecular assembly and in the modification of the physical properties of these materials (Williams *et al.*, 1985; Hudhomme *et al.*, 2001; Rovira & Novoa, 1999). We have



previously reported some radical salts with S \cdots S and C \cdots C intermolecular contacts (Lu *et al.*, 2006, 2007). In this report, a new salt of 2,3-bis(amide)-8,9-bis(methylsulfanyl)tetrathiafulvalene, $[\text{DMT-TTF}(\text{CONH}_2)_2]_2[\text{Cu}_2\text{Br}_4]$, (I), is described,

together with the intra- and intermolecular interactions in its structure.

Radical or charge-transfer salts are usually prepared by two techniques. The majority are obtained by electrocrystallization and the rest through chemical oxidation. The chemical oxidation method typically utilizes halogens and a number of transition metal salts in their higher oxidation state (*e.g.* Cu^{II} , Fe^{III} and Hg^{II}). In the preparation of (I), the TTF moiety of the precursor, $\text{DMT-TTF}(\text{CONH}_2)_2$, was oxidized by one electron during the reaction by a Cu^{II} salt which is reduced to Cu^{I} , forming a dinuclear anion.

The title compound, (I), is a radical cation salt with $[\text{Cu}_2\text{Br}_4]^{2-}$ anions and coupled $[\text{DMT-TTF}(\text{CONH}_2)_2]^+$ cations (Fig. 1). Both cation and anion are essentially planar. The two Cu^{I} ions are bridged by two bromide ions across a centre of inversion, to form a dinuclear anion with the Cu atom in a triangular coordination environment. As expected, the terminal Cu1–Br2 bonds are a little shorter than the bridging Cu1–Br1 bonds, which themselves differ slightly (Table 1). To the best of our knowledge, this structure of the $[\text{Cu}_2\text{Br}_4]^{2-}$ anion has not been reported in TTF salts to date; most such salts are further coordinated and the Cu^{I} centre adopts a tetrahedral geometry (Moustarder *et al.*, 2002; Kanehama *et al.*, 2003).

In the TTF units of (I), the central C=C bond distance [$\text{C3}=\text{C4} = 1.376(4) \text{ \AA}$] is longer than that found in neutral TTF compounds and is in agreement with that of $\text{TTF}^{+\cdot}$ radicals (Lu *et al.*, 2007). The IR stretching band of the central C=C bond at 1347 cm^{-1} shows a red shift relative to 1403 cm^{-1} for the neutral compound. It is known that the central C=C stretching of TTF undergoes a large frequency shift on oxidation ($>50\text{--}100 \text{ cm}^{-1}$) (Siedle *et al.*, 1980; Matsubayashi *et al.*, 1988). There is an intramolecular N–H \cdots O hydrogen bond between the two *ortho*-amide groups (Fig. 1 and Table 2).

Compound (I) crystallizes in the triclinic system, with one $[\text{DMT-TTF}(\text{CONH}_2)_2]_2[\text{Cu}_2\text{Br}_4]$ formula in the unit cell (the asymmetric unit consists of one $\text{TTF}^{+\cdot}$ cation and one half of a $[\text{Cu}_2\text{Br}_4]^{2-}$ anion). The cations are paired across centres of inversion to form a dimeric structure in a head-to-tail mode *via* short S \cdots S stacking interactions (Fig. 1). The S \cdots S distances of $3.339(1) [\text{S3}\cdots\text{S4}^{\text{vii}}$, symmetry code: (vii) $-x, -y - 1, -z + 1$;

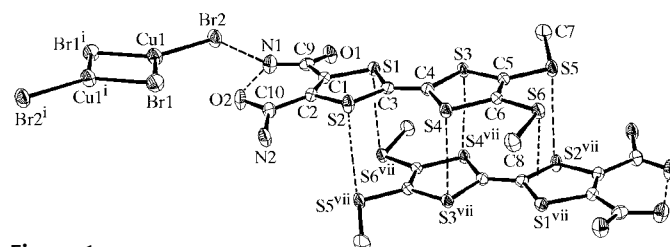


Figure 1

The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Intermolecular S \cdots S interactions in the TTF dimer and intramolecular N–H \cdots O hydrogen bonds are shown as dashed lines. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y - 1, -z + 1$; (vii) $-x, -y + 1, -z + 2$.]

$-y + 1, -z + 2]$, 3.419 (1) (S1 \cdots S6^{viii}) and 3.515 (1) Å (S2 \cdots S5^{vii}) indicate very effective stacking within the TTF dimer. The dimers further assemble into a one-dimensional step structure along the [010] direction through interdimer S \cdots S contacts between methylsulfanyl units [S5 \cdots S6^{viii} = 3.348 (1) Å; symmetry code: (viii) $-x, -y + 2, -z + 2]$ (Fig. 2). These one-dimensional chains then give rise to a two-dimensional structure in the (011) plane through interchain double N—H \cdots O hydrogen bonds (Fig. 3). Fig. 4 shows the co-operation of the hydrogen bonds and the S \cdots S contacts. The [Cu₂Br₄]²⁻ anions are located between the (011) planes and linked to two cations through Br \cdots H—N hydrogen bonds (Table 2).

It is noteworthy that no short intermolecular C \cdots C contact involving the central C=C bond was found within the TTF dimer. The electron paramagnetic resonance spectrum shows a radical signal ($g = 2.003$), which means that the two TTF^{•+}

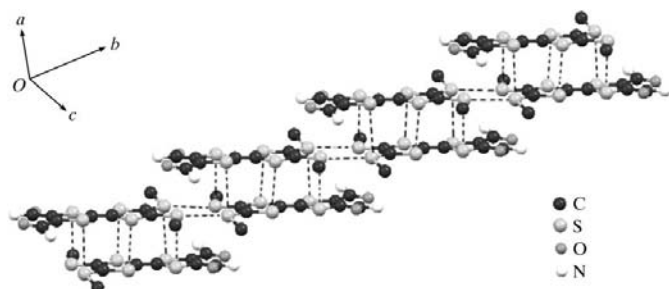


Figure 2
The assembly of the molecular couples in (I) into a one-dimensional step structure *via* intermolecular double S \cdots S contacts (dashed lines).

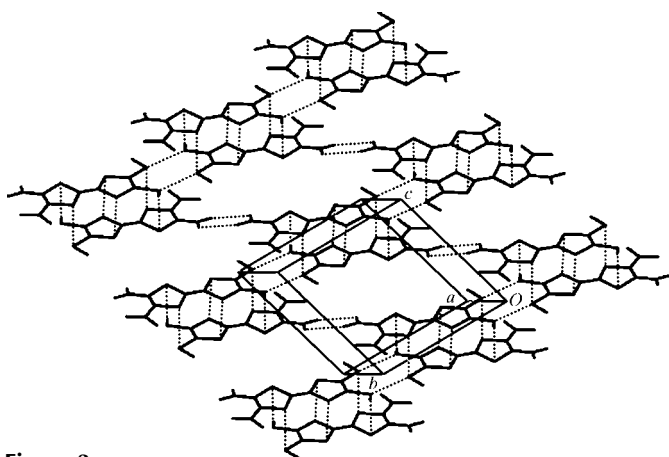


Figure 3
The packing of the TTF cations, showing the two-dimensional structure. Intermolecular contacts are shown as dotted lines. The [Cu₂Br₄]²⁻ anions are located between these layers, which stack along the *a* axis.

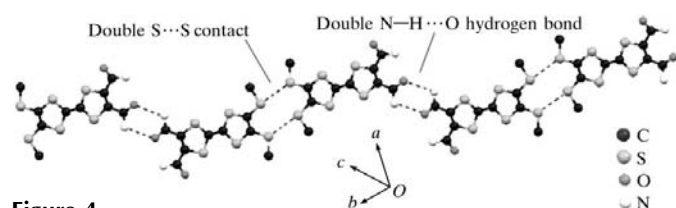


Figure 4
The co-operation of the double N—H \cdots O hydrogen bonds and double S \cdots S contacts in the molecular assembly of (I).

radicals are not completely coupled in the dimer. This result is in accordance with the conclusion in our earlier paper (Lu *et al.*, 2007), namely that the short intermolecular C \cdots C contact in the centre of the TTF moiety is the most important indicator of the coupling of the two radicals.

Experimental

The precursor 2,3-bis(methoxycarbonyl)-8,9-bis(methylsulfanyl)-tetrathiafulvalene was synthesized using a reported coupling method (Baudron *et al.*, 2003). Neutral 2,3-bis(aminocarbonyl)-8,9-bis(methylsulfanyl)tetrathiafulvalene, DM-TTF(CONH₂)₂, was obtained by reaction of the bis(methoxycarbonyl) derivative with ammonia (Hudhomme *et al.*, 2001; McCullough *et al.*, 1999). Compound (I) was obtained by careful addition of a solution of CuBr₂ (44.6 mg, 0.2 mmol) in acetonitrile (6 ml) to a solution of 2,3-bis(aminocarbonyl)-8,9-bis(methylsulfanyl)tetrathiafulvalene (7.6 mg, 0.02 mmol) in tetrahydrofuran (5 ml) in a straight tube (7 mm in diameter). The glass tube was sealed and the two solutions were kept unmixed. After 3 d, black crystals of (I) suitable for X-ray crystallographic analysis were obtained at the interface of the two phases. These were washed with acetonitrile and dried *in vacuo* (yield 15.90 mg, 66%). IR (KBr disc, ν , cm⁻¹): 3419 (NH), 3157 (NH), 1665 (C=O), 1347 (C=C). Analysis calculated for C₂₀H₂₀Br₄Cu₂N₄O₄S₁₂: C 19.80, H 1.65, N, 4.62%; found: C 19.63, H 1.51, N 4.50%.

Crystal data

(C ₁₀ H ₁₀ N ₂ O ₂ S ₆) ₂ [Cu ₂ Br ₄]	$\gamma = 81.242$ (7) ^o
$M_r = 1211.84$	$V = 895.25$ (14) Å ³
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.3326$ (9) Å	Mo $K\alpha$ radiation
$b = 10.0980$ (9) Å	$\mu = 6.39$ mm ⁻¹
$c = 10.3272$ (9) Å	$T = 173$ (2) K
$\alpha = 75.343$ (7) ^o	$0.30 \times 0.16 \times 0.15$ mm
$\beta = 72.571$ (6) ^o	

Data collection

Rigaku Mercury diffractometer	8740 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	3252 independent reflections
$T_{\min} = 0.218$, $T_{\max} = 0.383$	2819 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	211 parameters
$wR(F^2) = 0.070$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\max} = 0.70$ e Å ⁻³
3252 reflections	$\Delta\rho_{\min} = -0.61$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—Br1	2.3895 (6)	Cu1—Br1 ⁱ	2.4601 (6)
Cu1—Br2	2.3129 (6)	Cu1—Cu1 ⁱ	2.6149 (8)
Cu1—Br1—Cu1 ⁱ	65.24 (2)	Br2—Cu1—Br1 ⁱ	116.82 (2)
Br2—Cu1—Br1	128.38 (2)	Br1—Cu1—Br1 ⁱ	114.760 (19)

Symmetry code: (i) $-x + 1, -y - 1, -z + 1$.

H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters [N—H = 0.88 Å and C—H = 0.98 Å; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{C})$].

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...Br2	0.88	2.72	3.601 (3)	180
N1—H1B...O2	0.88	1.90	2.717 (4)	154
N2—H2A...O2 ⁱⁱ	0.88	2.09	2.951 (4)	167
N2—H2B...S2	0.88	2.44	2.906 (3)	114
N2—H2B...Br1 ⁱⁱⁱ	0.88	2.88	3.317 (3)	112
C7—H7A...Br2 ^{iv}	0.98	2.90	3.870 (4)	172
C7—H7B...S1 ^v	0.98	2.81	3.529 (3)	131
C7—H7C...Br2 ^{vi}	0.98	2.92	3.880 (4)	165
C8—H8B...O1 ⁱⁱⁱ	0.98	2.49	3.216 (4)	130
C8—H8C...Br2 ⁱⁱⁱ	0.98	2.99	3.648 (3)	126

Symmetry codes: (ii) $-x, -y, -z + 1$; (iii) $x - 1, y + 1, z$; (iv) $-x + 1, -y, -z + 2$; (v) $-x + 1, -y + 1, -z + 2$; (vi) $x, y + 1, z$.

molecular graphics: *ORTEP-32* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2007).

This work was supported by the National Natural Science Foundation of China (grant No. 20371033) and the Natural Science Foundation of the Education Committee of Jiangsu Province (grant No. 06KJB150102), China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3096). Services for accessing these data are described at the back of the journal.

References

- Baudron, S. A., Avarvari, N., Batail, P., Coulon, C., Clérac, R., Canadell, E. & Auban-Senzier, P. (2003). *J. Am. Chem. Soc.* **125**, 11583–11590.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hudhomme, P., Le Moustarder, S., Durand, C., Gallego-Planas, N., Mercier, N., Blanchard, P., Levillain, E., Allain, M., Gorgues, A. & Riou, A. (2001). *Chem. Eur. J.* **7**, 5070–5083.
- Jacobson, R. (1998). Private communication to Rigaku Corporation, Tokyo, Japan.
- Kanehama, R., Umemiya, M., Iwahori, F., Miyasaka, H., Sugiura, K., Yamashita, M., Yokochi, Y., Ito, H., Kuroda, S., Kishida, H. & Okamoto, H. (2003). *Inorg. Chem.* **42**, 7173–7181.
- Lu, W., Zhang, Y., Dai, J., Zhu, Q.-Y., Bian, G.-Q. & Zhang, D.-Q. (2006). *Eur. J. Inorg. Chem.* pp. 1629–1634.
- Lu, W., Zhu, Q.-Y., Dai, J., Zhang, Y., Bian, G.-Q., Liu, Y. & Zhang, D.-Q. (2007). *Cryst. Growth Des.* **7**, 652–657.
- McCullough, R. D., Petruska, M. A. & Belot, J. A. (1999). *Tetrahedron*, **55**, 9979–9998.
- Matsubayashi, G., Yokoyama, K. & Tanaka, T. (1988). *J. Chem. Soc. Dalton Trans.* pp. 3059–3062.
- Moustarder, S., Mercier, N., Hudhomme, P., Gallego-Planas, N., Gorgues, A. & Riou, A. (2002). *Synth. Met.* **130**, 129–134.
- Rigaku (2001). *CrystalClear* and *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
- Rovira, C. & Novoa, J. J. (1999). *Chem. Eur. J.* **5**, 3689–3697.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siedle, A. R., Kistenmacher, T. J., Metzger, R. M., Kuo, C. S., van Duyne, R. P. & Cape, T. (1980). *Inorg. Chem.* **19**, 2048–2051.
- Westrip, S. P. (2007). *publCIF*. In preparation.
- Williams, J. M., Beno, M. A., Wang, H. H., Leung, P. C. W., Emge, T. J., Geiser, U. & Carlson, K. D. (1985). *Acc. Chem. Res.* **18**, 261–267.