Fig. 1. *ORTEP* (Johnson, 1976) drawing and numbering scheme. The ellipsoids are drawn at the 30% probability surface and H atoms have been given arbitrary radii for figure clarity.

features of sulfur dioxide complexes in general have been reviewed by Ryan, Kubas, Moody & Eller (1981).

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Structures of Two Bis(ethylenedithio)tetrathiafulvalene Hexamolybdate and Hexatungstate Salts: (BEDT-TTF)₂M_6O_{19}, M= Mo, W

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Abstract. $2C_{10}H_8S_8^+ \cdot Mo_6O_{19}^{2-}$ (1), $M_r = 1649$, monoclinic, $P2_1/c$, $a = 8.898$ (8), $b = 11.265$ (4), $c = 21.098$ (8) Å, $\beta = 96.34$ (5)°, $V = 2102$ Å³, $Z = 2$, $D_x = 2.605$ g cm⁻³, $F(000) = 1592$, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 25.33$ cm⁻¹, $T = 293$ K, $R = 0.036$ based on 1527 observed reflections with $I \geq 3\sigma(I)$. $2C_{10}H_8S_8^+ \cdot W_6O_{19}^{2-}$ (2), $M_r = 2176.46$, monoclinic, $P2_1/c$, $a = 8.908$ (7), $b = 11.310$ (5), $c = 21.111$ (8) Å, $\beta = 96.37$ (7)°, $V = 2113.8$ Å³, $Z = 2$, $D_x = 3.419$ g cm⁻³. Only the structure of (1) has been determined since the two compounds are isostructural. The central C=C (1.388 Å) and the two types of C—S (average 1.720 and 1.737 Å) bond lengths of the BEDT-TTF molecule compare well with those observed for one which is fully oxidized. As in the κ-(BEDT-TTF)₂X salts, the organic radical cations form orthogonalized dimers (dihedral angle 76°). Short intra-dimer (S1···S4 3.551 and S2···S3 3.553 Å) and inter-dimer (S7···S8 3.508 Å) S···S contacts are observed. The crystal structure is built by alternating *ABABA*... organic and inorganic layers along the [100] direction.

Experimental. The compounds were obtained on a platinum-wire electrode by anodic oxidation of DMF (DMF = *N,N*-dimethylformamide) solutions of the organic donor (BEDT-TTF) ($2 \times 10^{-3}M$), under low constant current ($I = 1.25$ μA) in the presence of the tetrabutylammonium salts of the $[M_6O_{19}]^{2-}$ dianions ($10^{-2}M$) as supporting electro-

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Table 1. *Atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Mo1	0.2160 (1)	−0.01337 (8)	−0.05274 (4)	2.34 (2)
Mo2	−0.1205 (1)	−0.13820 (8)	−0.06937 (4)	2.24 (2)
Mo3	−0.0920 (1)	0.15180 (8)	−0.06764 (5)	2.37 (2)
O1	0.0763 (8)	−0.1274 (6)	−0.0965 (3)	2.5 (2)
O2	0.0933 (8)	0.1068 (6)	−0.0998 (3)	2.4 (2)
O3	−0.163 (1)	0.2575 (7)	−0.1194 (4)	2.9 (2)
O4	−0.1750 (8)	0.0050 (6)	−0.1106 (4)	2.4 (2)
O5	−0.0184 (9)	−0.2362 (6)	0.0027 (4)	2.7 (2)
O6	−0.2678 (8)	−0.1064 (6)	−0.0105 (4)	2.5 (2)
O7	0.3699 (9)	−0.0222 (8)	−0.0920 (4)	3.7 (2)
O8	−0.2056 (9)	−0.2422 (7)	−0.1201 (4)	3.3 (2)
O9	0.2507 (9)	−0.1295 (7)	0.0130 (4)	3.2 (2)
O10	0	0	0	1.5 (2)
S1	0.1623 (3)	0.5104 (3)	−0.0596 (1)	2.40 (6)
S2	0.3429 (3)	0.3095 (2)	−0.0924 (1)	2.15 (6)
S3	0.3214 (3)	0.5173 (2)	0.0785 (1)	2.41 (6)
S4	0.5086 (4)	0.3103 (3)	0.0565 (1)	2.39 (6)
S5	−0.0206 (4)	0.5308 (3)	−0.1827 (2)	2.90 (7)
S6	0.1973 (4)	0.2917 (3)	−0.2262 (2)	3.33 (7)
S7	0.4264 (4)	0.5424 (3)	0.2144 (1)	3.53 (8)
S8	0.6412 (4)	0.2866 (3)	0.1896 (2)	3.94 (8)
C1	0.301 (1)	0.4089 (9)	−0.0357 (5)	2.2 (2)
C2	0.375 (1)	0.4149 (9)	0.0258 (5)	1.8 (2)
C3	0.213 (1)	0.3647 (9)	−0.1521 (5)	2.4 (2)
C4	0.127 (1)	0.4562 (9)	−0.1371 (5)	1.9 (2)
C5	0.435 (1)	0.4614 (9)	0.1442 (5)	2.3 (2)
C6	0.521 (1)	0.3659 (9)	0.1336 (5)	2.3 (2)
C7	−0.031 (2)	0.455 (1)	−0.2588 (5)	3.5 (3)
C8	0.004 (1)	0.323 (1)	−0.2531 (6)	2.6 (3)
C9	0.532 (2)	0.447 (2)	0.2703 (6)	7.2 (5)
C10	0.635 (2)	0.370 (2)	0.2558 (8)	11.4 (5)

Table 2. *Bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses*

Mo1—O1	1.948 (7)	S2—C3	1.730 (11)
Mo1—O2	1.941 (7)	S3—C2	1.705 (11)
Mo1—O6	1.917 (7)	S3—C5	1.741 (11)
Mo1—O7	1.680 (9)	S4—C2	1.748 (11)
Mo1—O9	1.907 (7)	S4—C6	1.735 (11)
Mo1—O10	2.330 (1)	S5—C4	1.756 (11)
Mo2—O1	1.905 (8)	S5—C7	1.815 (12)
Mo2—O4	1.871 (7)	S6—C3	1.759 (11)
Mo2—O5	2.012 (7)	S6—C8	1.787 (12)
Mo2—O6	1.937 (8)	S7—C5	1.749 (11)
Mo2—O8	1.706 (8)	S7—C9	1.79 (2)
Mo2—O10	2.317 (1)	S8—C6	1.751 (11)
Mo3—O2	1.919 (8)	S8—C10	1.69 (2)
Mo3—O3	1.689 (7)	C1—C2	1.388 (14)
Mo3—O4	1.989 (7)	C3—C4	1.340 (15)
Mo3—O5	1.857 (7)	C5—C6	1.350 (15)
Mo3—O9	1.935 (8)	C7—C8	1.52 (2)
Mo3—O10	2.318 (1)	C9—C10	1.31 (3)
S1—C1	1.718 (11)		
S1—C4	1.741 (10)		
S2—C1	1.710 (11)		

O1—Mo1—O2	85.6 (3)	O5—Mo3—O9	89.3 (3)
O1—Mo1—O6	152.3 (3)	O5—Mo3—O10	78.5 (2)
O1—Mo1—O7	103.8 (4)	O9—Mo3—O10	76.6 (2)
O1—Mo1—O9	86.3 (3)	Mo1—O1—Mo2	117.3 (4)
O1—Mo1—O10	75.6 (2)	Mo1—O2—Mo3	117.4 (4)
O2—Mo1—O6	86.8 (3)	Mo2—O4—Mo3	116.1 (3)
O2—Mo1—O7	103.4 (4)	Mo2—O5—Mo3	115.8 (4)
O2—Mo1—O9	152.5 (3)	Mo1—O6—Mo2	116.7 (4)
O2—Mo1—O10	75.6 (2)	Mo1—O9—Mo3	116.9 (4)
O6—Mo1—O7	103.8 (4)	Mo1—O10—Mo2	89.90 (4)
O6—Mo1—O9	88.3 (3)	Mo1—O10—Mo3	89.56 (4)
O6—Mo1—O10	76.7 (2)	Mo2—O10—Mo3	89.97 (3)
O7—Mo1—O9	104.1 (4)	C1—S1—C4	95.3 (5)
O7—Mo1—O10	178.9 (3)	C1—S2—C3	95.4 (5)
O9—Mo1—O10	76.9 (3)	C2—S3—C5	95.4 (5)
O1—Mo2—O4	90.3 (3)	C2—S4—C6	94.2 (5)
O1—Mo2—O5	84.8 (3)	C4—S5—C7	102.7 (6)
O1—Mo2—O6	152.9 (3)	C3—S6—C8	99.7 (6)
O1—Mo2—O8	102.4 (4)	C5—S7—C9	100.1 (7)
O1—Mo2—O10	76.7 (2)	C6—S8—C10	101.5 (8)
O4—Mo2—O5	153.7 (3)	S1—C1—S2	115.8 (6)
O4—Mo2—O6	88.8 (3)	S1—C1—C2	119.5 (8)
O4—Mo2—O8	103.0 (3)	S2—C1—C2	124.7 (8)
O4—Mo2—O10	78.0 (2)	S3—C2—S4	116.2 (6)
O5—Mo2—O6	84.1 (3)	S3—C2—C1	120.3 (8)
O5—Mo2—O8	103.3 (3)	S4—C2—C1	123.1 (8)
O5—Mo2—O10	75.7 (2)	S2—C3—S6	117.4 (7)
O6—Mo2—O8	104.2 (4)	S2—C3—C4	117.2 (8)
O6—Mo2—O10	76.6 (2)	S6—C3—C4	125.3 (8)
O8—Mo2—O10	178.6 (3)	S1—C4—S5	113.1 (6)
O2—Mo3—O3	103.3 (4)	S1—C4—C3	116.3 (8)
O2—Mo3—O4	84.8 (3)	S5—C4—C3	130.6 (8)
O2—Mo3—O5	89.5 (3)	S3—C5—C7	114.2 (6)
O2—Mo3—O9	152.6 (3)	S3—C5—C6	116.4 (8)
O2—Mo3—O10	76.3 (2)	S7—C5—C6	129.3 (8)
O3—Mo3—O4	101.5 (3)	S4—C6—S8	114.7 (6)
O3—Mo3—O5	104.2 (3)	S4—C6—C5	117.7 (8)
O3—Mo3—O9	103.5 (4)	S8—C6—C5	127.6 (9)
O3—Mo3—O10	177.3 (3)	S5—C7—C8	113.7 (8)
O4—Mo3—O5	154.4 (3)	S6—C8—C7	113.5 (9)
O4—Mo3—O9	84.6 (3)	S7—C9—C10	125.1 (1)
O4—Mo3—O10	75.8 (2)	S8—C10—C9	130.1 (1)

lyte. The latter were prepared according to literature procedures (Che, Fournier & Launay, 1979; Sanchez, Livage, Launay & Fournier, 1983).

A black crystal with approximate dimensions $0.8 \times 0.16 \times 0.16$ mm was selected for intensity data collection carried out on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation. θ–2θ scans. Cell dimensions: least-squares refinement from setting angles of 25 centered reflections ($\theta \leq 15°$). Three standard reflections measured every hour: no fluctuations in intensities. 4624 reflections were recorded in the range $2 \leq 2\theta \leq 50°$, with $0 \leq h \leq 10$, $0 \leq k \leq 13$, $-25 \leq l \leq 25$. Lorentz–polarization and an empirical absorption correction were applied using the *DIFABS* procedure (Walker & Stuart, 1983). The minimum and maximum correction factors were 0.803 and 1.061. The structure was solved by the heavy-atom method and successive Fourier difference syntheses. 1527 independent reflections with $I \geq 3\sigma(I)$, after averaging of symmetry-related reflections ($R_{int} = 0.071$), were used for the refinements. H atoms placed at computed positions $[d(\text{C—H}) = 1.0 \text{ Å}; B_{eq} = 4.0 \text{ Å}^2]$. Full-matrix least-squares anisotropic (β_{ij}) refinement on F^2, H atoms isotropic not refined; secondary extinction refined, $g = 5.49 \times 10^{-9}$. $R = 0.036$, $wR = 0.044$, $w = 4F_o^2/[\sigma^2(F_o^2) + (0.06F_o^2)^2]$, $S = 1.08$, $(\Delta/\sigma)_{max} = 0.05$, $\Delta\rho_{max} = 0.628 \text{ e Å}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All the calculations were

performed on a PDP11/60 using the *SDP* programs (B. A. Frenz & Associates, Inc., 1985). Final atomic positional and thermal parameters are given in Table 1,* and bond lengths and bond angles in Table 2. The atomic numbering and the intra-dimer overlap are shown in Fig. 1. The evidence of orthogonalized

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53542 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

fully oxidized dimers and a stereoview of the crystal structure are presented in Figs. 2 and 3, respectively.

Related literature. This work continues our research in the area of Organic Donor Inorganic Acceptor (ODIA) charge-transfer salts (Ouahab, Bencharif & Grandjean, 1988; Triki, Ouahab, Padiou & Grand-
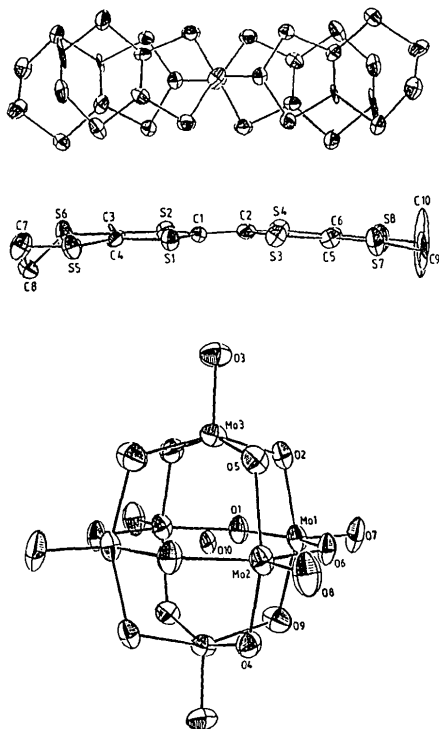

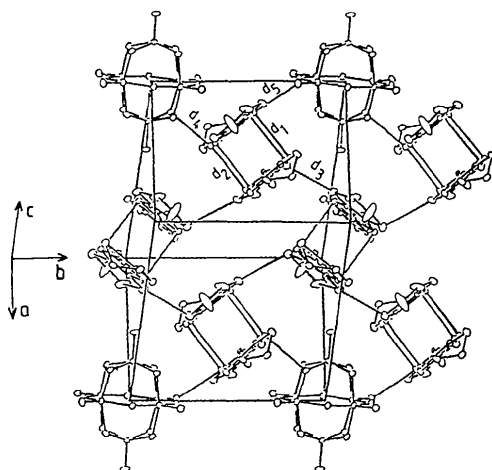Fig. 1. Atomic numbering, intra-dimer overlap and configuration of the donor.

Fig. 2. Projection of the structure showing orthogonalized dimers. $d1(S1—S4^i) = 3.551$ (5), $d2(S2—S3^i) = 3.553$ (5), $d3(S7—S8^{ii}) = 3.508$ (5), $d4(S2—O2) = 3.177$ (8), $d5(S3—O3^{iii}) = 3.074$ (8) Å. Symmetry code: (i) $1-x$, $1-y$, $-z$; (ii) $1-x$, y, $-z$; (iii) $-x$, $1-y$, $-z$.

Table 3. *Comparison of the averaged intramolecular distances* (Å) *for various observed charges on the* BEDT-TTF *molecule*

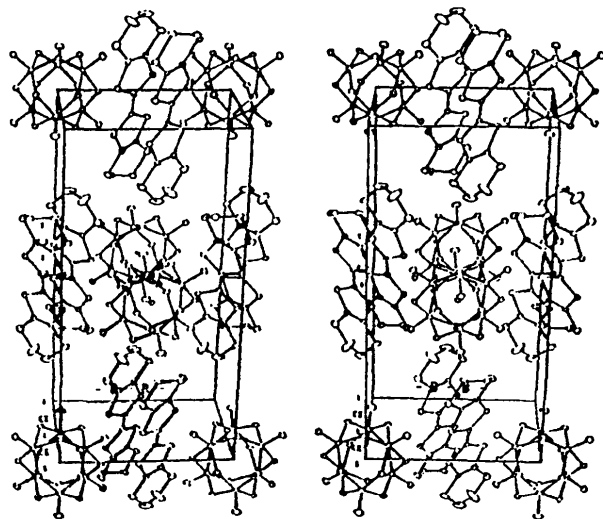| Compound	Charge	a	b	c	d
BEDT-TTF	0	1.319	1.757	1.753	1.331
$(BEDT-TTF)_2FeCl_4$	$+\frac{1}{2}$	1.360	1.732	1.744	1.340
$(BEDT-TTF)_3ZnCl_4$	$+1$	1.373	1.721	1.736	1.349
$(BEDT-TTF)_2Mo_6O_{19}$	$+1$	1.388	1.720	1.737	1.345
$(BEDT-TTF)_3ZnCl_4$	$+2$	1.436	1.669	1.710	1.369

Fig. 3. Stereoscopic view of the crystal structure.

jean, 1989). The $M_6O_{19}^{2-}$ polyanions are members of a group of discrete isopolymetallates having a Lindquist type structure (Lindquist, 1953).

The general structural features of the $[Mo_6O_{19}]^{2-}$ unit [average Mo—Mo 3.286 (2), Mo—O$_t$ 1.692 (8), Mo—O$_b$ 1.928 (8) and Mo—O$_c$ 2.322 (1) Å] are in good agreement with those reported in $[HN_3P_3(NMe_2)_6]_2[Mo_6O_{19}]$, for example (Allcock, Bissell & Shawl, 1973).

The charge on the BEDT-TTF moiety has been assumed to be $+1$ on the basis of the comparison (Table 3) of its geometrical parameters with those found for a variety of oxidation states of the molecule, *e.g.* BEDT-TTF^0 (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1986), BEDT-TTF$^{0.5+}$ (Mallah, Hollis, Bott, Kurmoo, Day, Allan & Friend, 1990), BEDT-TTF$^+$ and BEDT-TTF^{2+} (Shibaeva, Lobkovskaya, Korotkov, Kushch, Yagubskii & Makova, 1988). The orthogonalized organic dimers arrangement (Fig. 2) is similar to that observed in the superconducting κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ phase (Urayama *et al.*, 1987). The dihedral angle between adjacent dimers is 76.29°. The structure can be described by alternating layers

of organic and inorganic entities of the *ABABA*... type of packing. Intermolecular interactions are observed through short S···S (≤ 3.60 Å) and S···O (≤ 3.20 Å) contacts (see Fig. 2).

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[(C₅Me₅)(Et₂NCS₂)Rh(μ-Ph₂PCH₂CH₂PPh₂)Rh(Et₂NCS₂)(C₅Me₅)]²⁺.2BPh₄⁻

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Abstract. [μ-Ethylenebis(diphenylphosphine)-1κP:-2κP]-bis[(N,N-diethyldithiocarbamato)(η⁵-pentamethylcyclopentadienyl)rhodium(III)] bis(tetraphenylborate), [Rh₂(C₁₀H₁₅)₂(C₅H₁₀NS₂)₂(C₂₆H₂₄P₂)]²⁺. 2C₂₄H₂₀B⁻, $M_r = 1809.7$, orthorhombic, *Pbca*, $a = 28.497$ (9), $b = 19.236$ (8), $c = 16.700$ (9) Å, $V = 9154$ Å³, $Z = 4$, $D_x = 1.31$ Mg m⁻³, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.492$ mm⁻¹, $F(000) = 3784$, $T = 295$ K, $R = 0.0598$ for 5198 unique observed reflections. The dication is centrosymmetric, the two [C₅Me₅Rh(S₂CNEt₂)] units being linked by a Ph₂PCH₂—CH₂PPh₂ ligand whose midpoint lies on a crystallographic inversion centre.

Experimental. Title compound prepared by reaction of [C₅Me₅Rh(S₂CNEt₂)Cl] with Ph₂PCH₂CH₂PPh₂ (dppe) in CH₂Cl₂ followed by the addition of NaBPh₄ in MeOH, crystals obtained by crystallization from MeOH. Orange sphenoid, $0.2 \times 0.3 \times 1.4$ mm, mounted to rotate about c on Stoe STADI-2 two-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from nine $hk0$ and

four $00l$ reflections. For data collection, ω scans with ω-scan width $(1.0 + 0.50\tan\theta)°$, $2\theta_{max} = 50°$, h 0→32, k 0→22, l 0→19, no significant crystal movement or decay, 8127 reflections collected, 7936 unique ($R_{int} = 0.039$), giving 5198 with $F \geq 6\sigma(F)$ for
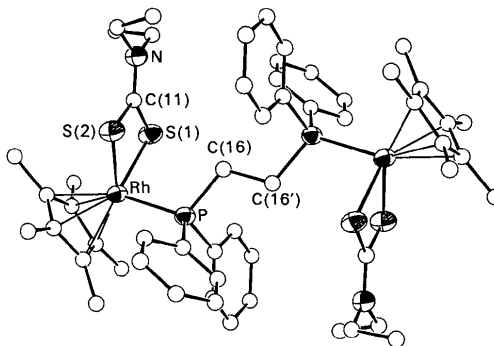

Fig. 1. A general view of the dication showing atom-numbering scheme: H atoms have been removed for clarity. Thermal ellipsoids are drawn at the 30% probability level, except those of C atoms which have artificial radii of 0.15 Å. The dication is centrosymmetric; the midpoint of the CH₂—CH₂ bond in the dppe ligand lies on an inversion centre.

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