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A Novel Type of Two-Dimensional Pattern of Association of Mixed-Valence Dimers in the Structures of Two Cation Radical Salts of Thieno- and Selenolo[3,4-*d*]-1,3-dithiol-2-ylidene and a Monovalent Hexanuclear Chalcohalide Rhenium Cluster Anion

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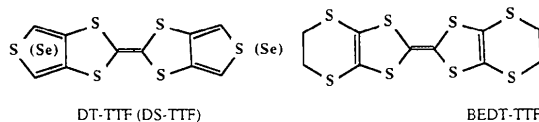
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Abstract. 2,2'-Bi(thieno[3,4-*b*]-1,3-dithiol-2-ylidene) nonachloropentathiahexarhenate-dimethylformamide (1/2), (2C₁₀H₄S₆)⁺.Re₆S₅Cl₉⁻.2C₃H₇NO (1), *M_r* = 2375.84, triclinic, *P* $\bar{1}$, *a* = 9.220 (5), *b* = 11.493 (2), *c* = 12.433 (3) Å, α = 102.74 (2), β = 90.82 (3), γ = 93.25 (3)°, *V* = 1282 (6) Å³, *Z* = 1, *D_x* = 3.079 g cm⁻³, *F*(000) = 1083, λ (Mo *K*α) = 0.70173 Å, μ = 154.9 cm⁻¹, *T* = 293 K, *R* = 0.029 based on 5662 observed reflections with *I* ≥ 3σ(*I*). 2,2'-Bi(selenolo[3,4-*b*]-1,3-dithiol-2-ylidene) nonachloropentathiahexarhenate-dimethylformamide (1/2), (2C₁₀H₄S₄Se₂)⁺.Re₆S₅Cl₉⁻.2C₃H₇NO (2), *M_r* = 2563.43, triclinic, *P* $\bar{1}$, *a* = 9.245 (1), *b* = 11.576 (2), *c* = 12.433 (2) Å, α = 102.75 (1), β = 90.72 (1), γ = 93.21 (1)°, *V* = 1295 (4) Å³, *Z* = 1, *D_x* = 3.286 g cm⁻³, *F*(000) = 1155, λ (Mo *K*α) = 0.71073 Å, μ = 179.5 cm⁻¹, *T* = 293 K, *R* = 0.026 based on 4636 observed reflections with *I* ≥ 3σ(*I*). The two compounds are isostructural. Single layers of organic cation radical molecules and inorganic cluster anions alternate along *c* with dimethylforma-

mid (DMF) molecules locked into the lattice *via* a set of C—H...O hydrogen bonds. The compounds are insulating and the organic dimer spins are essentially localized and non-interacting within the organic donor slab which has an unprecedented configuration.

Introduction. A wealth of novel architectures, associated with specific conducting and magnetic properties, has been unravelled for new families of cation radical salts where tetrathiafulvalene and several of its substituted derivatives are associated with large fully inorganic molecular anions (Pénicaud, Boubekeur, Batail, Canadell, Auban-Senzier & Jérôme, 1993, and references therein). The present paper describes the structure and magnetic properties of two such salts of organic-inorganic character based on organic donor molecules bearing, on each side, a single exposed chalcogen atom. In contrast to the more commonly used organic donor molecules such as bis(ethylenedithio)tetrathiafulvalene (BEDT-

TTF), the presence of only two outer S or Se atoms in DT-TTF and DS-TTF, respectively, located in the symmetry plane of the molecule is expected to induce novel patterns of intermolecular interactions as demonstrated in this paper.



Experimental. DT-TTF (Chiang, Shu, Holt & Cowan, 1983; Santalo, Veciana, Rovira, Molins, Miravittles & Claret, 1991; Shu, Chiang, Emge, Holt, Kistenmacher, Lee, Stokes, Poehler, Bloch & Cowan, 1981) and DS-TTF (Ketcham, Hoernfeldt & Gronowitz, 1984) were synthesized according to known procedures. They were recrystallized from chlorobenzene prior to crystal growth. The title compounds were prepared by constant current (0.4 μ A, 15 d) oxidation at a platinum wire electrode in 8 ml of a 1:3 DMF:C₆H₅Cl solution (purified over activated alumina) containing the donor (2×10^{-2} mmol) and the tetrabutylammonium salt (Bu₄N)Re₆S₅Cl₉ (2.7×10^{-2} mmol) (Boubekur, 1989).

Data are given in the form (1) [(2)]. The intensity data were collected on an Enraf-Nonius CAD-4F diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The dimensions of the crystal fragment were $0.21 \times 0.15 \times 0.15$ mm ($0.24 \times 0.12 \times 0.15$ mm). The unit-cell dimensions and crystal-orientation matrix were obtained by a least-squares refinement of the setting angles of 25 reflections with $8 \leq \theta \leq 13.8^\circ$ ($8.0 \leq \theta \leq 16.0^\circ$). Intensity data were recorded in the range $1 \leq \theta \leq 29^\circ$ ($1 \leq \theta \leq 28^\circ$) with $0 \leq h \leq 12$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$ ($-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $0 \leq l \leq 16$); ω - θ (ω - $\theta/3$) scan method was used with scan width $\Delta\omega = (0.9 + 0.35\tan\theta)^\circ$ [$\Delta\omega = (1.1 + 0.35\tan\theta)^\circ$] extended 25% on each side for background measurement, and horizontal counter aperture $\Delta\lambda = (1.4 + 0.5\tan\theta)$ mm [$\Delta\lambda = (1.8 + 0.5\tan\theta)$ mm], vertical aperture 4 mm, prescan speed $8.24^\circ \text{ min}^{-1}$ ($16.48^\circ \text{ min}^{-1}$), $\sigma(I)/I = 0.010$, maximum time for final scan 60 s. Three orientation and three intensity control reflections checked every 500 reflections (maintained within 0.10°) and every hour, respectively, showed no significant variation in intensity. The data were corrected for Lorentz and polarization effects and for absorption based on ψ -scan data obtained at the conclusion of intensity-data collection. The minimum relative transmission was 84.9% (65.56%); the minimum and maximum absorption factors were 0.92 (1.00) and 0.99 (1.06), respectively, with an average value of 0.96 (1.03). 7205 (6521) reflections

measured of which 6389 (5955) were unique [$R_{\text{int}} = 0.017$ (0.022)]. 5662 (4636) reflections with $I > 3\sigma(I)$ were considered observed and used in the calculations. The metal atoms were located by Patterson synthesis. All remaining non-H atoms were obtained by the application of alternating full-matrix least-squares refinements and difference Fourier syntheses. H atoms placed at computed positions [$d(\text{C}-\text{H}) = 0.95 \text{ \AA}$, $B_{\text{eq}} = 1.3 \times B_{\text{eq}}(\text{C})$]. Five S and three Cl atoms were disordered on the eight ligand positions of the anion and were refined as mixed atoms $L = 0.375 \text{ Cl} + 0.625 \text{ S}$. All non-H atoms were finally refined with anisotropic thermal parameters. Expression minimized $\sum w(\Delta F)^2$ for 5662 (4636) reflections and 296 parameters. Final $R = 0.029$ (0.026), $wR = 0.044$ (0.041), $S = 1.077$ (0.963), $w = 1/[\sigma^2(F_o) + 0.05F_o^2]$, $(\Delta/\sigma)_{\text{max}} = 0.00$ (0.01), highest peak [ghost to Re(1)] in final difference Fourier synthesis 1.635 e \AA^{-3} (1.395 e \AA^{-3}). Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a DEC MicroVAX II using the Enraf-Nonius SDP program package (Frenz, 1985). ESR spectra were recorded on a Varian X-band spectrometer (frequency 9.3 GHz) equipped with an Oxford ESR 900 helium cryostat.

Discussion. The title compounds are isostructural. Fractional coordinates are listed in Table 1.* Bond lengths, selected bond angles and hydrogen-bond geometry are given in Table 2. Central to the structure are a set of chalcogen...chalcogen intermolecular contacts which are classified into three types S...S, S...X and X...X and listed in Table 3 where X denotes the outer chalcogen atoms, either S or Se, at the periphery of the central, common tetrathiafulvalene core (scheme). The asymmetric unit consists of one DT-TTF (DS-TTF) molecule, one-half cluster anion and one DMF molecule. The two centrosymmetrically related DMF molecules are not disordered in the crystal, rather, they are found to be properly locked in by a set of hydrogen bonds (Fig. 1), between the carbonyl O atom and one H atom of the donor molecule. The C(H)...O and (C)H...O distances between the donor C atoms and protons nearest the DMF carbonyl O atom and the CHO angles are given in Table 2. They are in agreement with the literature data for such C—H...O hydrogen bonds (Pénicaud, Lenoir, Batail, Coulon & Perrin,

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, root-mean-square amplitudes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55890 (69 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1024]

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses for (1) and (2)
$$B_{eq} = \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \beta_{ij}$$

	x	y	z	B _{eq}
Dimer (1)				
Re(1)	0.09874 (2)	0.07028 (2)	-0.09820 (2)	1.809 (4)
Re(2)	0.17229 (2)	-0.01480 (2)	0.06980 (2)	1.841 (4)
Re(3)	-0.01506 (2)	0.14684 (2)	0.09060 (2)	1.805 (4)
Cl(1)	0.2298 (2)	0.1665 (2)	-0.2209 (1)	3.40 (3)
Cl(2)	0.3988 (2)	-0.0304 (2)	0.1567 (1)	3.63 (3)
Cl(3)	-0.0358 (2)	0.3406 (1)	0.2034 (1)	3.33 (3)
L(1)*	0.2668 (2)	-0.0879 (1)	-0.1127 (1)	2.71 (3)
L(2)*	-0.0536 (2)	-0.0562 (1)	-0.2397 (1)	2.74 (3)
L(3)*	0.0819 (2)	-0.2152 (1)	0.0724 (1)	2.58 (3)
L(4)*	0.2385 (2)	0.1878 (1)	0.0591 (1)	3.04 (3)
S(1)	0.5546 (2)	0.6672 (2)	0.3932 (1)	2.95 (3)
S(2)	0.5421 (2)	0.7393 (2)	0.6363 (1)	3.47 (4)
S(3)	0.7272 (2)	0.5249 (2)	0.6586 (1)	3.08 (3)
S(4)	0.7700 (2)	0.4637 (2)	0.4179 (1)	2.76 (3)
S(5)	0.2887 (2)	0.9607 (2)	0.4876 (2)	4.03 (4)
S(6)	1.0249 (2)	0.2523 (2)	0.5794 (2)	3.56 (4)
C(1)	0.6058 (7)	0.6449 (5)	0.5192 (5)	2.5 (1)
C(2)	0.6940 (6)	0.5536 (6)	0.5319 (5)	2.6 (1)
C(3)	0.4466 (7)	0.7863 (6)	0.4438 (6)	2.9 (1)
C(4)	0.4421 (7)	0.8206 (6)	0.5612 (6)	3.0 (1)
C(5)	0.8488 (7)	0.4162 (6)	0.6137 (5)	2.7 (1)
C(6)	0.8656 (7)	0.3847 (5)	0.4965 (5)	2.61 (1)
C(7)	0.3661 (8)	0.8527 (6)	0.3932 (6)	3.7 (1)
C(8)	0.3586 (8)	0.9161 (7)	0.5966 (6)	3.6 (1)
C(9)	0.9286 (8)	0.3516 (6)	0.6682 (6)	3.3 (1)
C(10)	0.9611 (8)	0.2964 (6)	0.4666 (6)	3.4 (1)
O(1)	0.3588 (8)	0.6314 (6)	0.1801 (5)	5.7 (2)
N(1)	0.3503 (7)	0.5853 (6)	-0.0051 (5)	4.0 (1)
C(11)	0.3977 (9)	0.6474 (7)	0.0914 (7)	4.1 (2)
C(12)	0.411 (1)	0.615 (1)	-0.1069 (7)	6.2 (2)
C(13)	0.240 (1)	0.4884 (8)	-0.0163 (9)	6.3 (3)
Dimer (1)				
Re(1)	0.9998 (3)	0.06895 (2)	-0.09772 (2)	1.888 (5)
Re(2)	0.16973 (3)	-0.01347 (2)	0.07205 (2)	1.932 (5)
Re(3)	-0.01770 (3)	0.14623 (2)	0.08918 (2)	1.880 (5)
Cl(1)	0.2334 (3)	0.1642 (2)	-0.2194 (2)	3.43 (4)
Cl(2)	0.3928 (2)	-0.0281 (2)	0.1613 (2)	3.81 (4)
Cl(3)	-0.0399 (3)	0.3394 (2)	0.1998 (2)	3.51 (4)
L(1)*	0.2679 (2)	-0.0869 (2)	-0.1086 (2)	2.83 (4)
L(2)*	-0.0480 (2)	-0.0578 (2)	-0.2398 (1)	2.87 (4)
L(3)*	0.0815 (2)	-0.2116 (2)	0.0754 (2)	2.80 (4)
L(4)*	0.2357 (2)	0.1881 (2)	0.0604 (2)	3.21 (4)
Se(1)	0.2827 (1)	0.96701 (8)	0.48853 (9)	3.89 (2)
Se(2)	1.0355 (1)	0.24811 (8)	0.58255 (8)	3.48 (2)
S(1)	0.5520 (2)	0.6641 (2)	0.3938 (2)	2.81 (4)
S(2)	0.5417 (3)	0.7368 (2)	0.6366 (2)	3.38 (4)
S(3)	0.7302 (2)	0.5274 (2)	0.6598 (2)	2.99 (4)
S(4)	0.7687 (2)	0.4630 (2)	0.4195 (2)	2.71 (4)
C(1)	0.6062 (8)	0.6422 (7)	0.5212 (6)	2.4 (1)
C(2)	0.6952 (8)	0.5552 (6)	0.5316 (6)	2.1 (1)
C(3)	0.4453 (9)	0.7818 (7)	0.4471 (6)	2.5 (1)
C(4)	0.4417 (9)	0.8188 (7)	0.5644 (6)	2.6 (1)
C(5)	0.8509 (9)	0.4176 (7)	0.6153 (6)	2.7 (2)
C(6)	0.8661 (9)	0.3853 (7)	0.4973 (6)	2.6 (1)
C(7)	0.369 (1)	0.8497 (8)	0.3928 (7)	3.6 (2)
C(8)	0.364 (1)	0.9131 (8)	0.6016 (8)	3.6 (2)
C(9)	0.9285 (9)	0.3574 (8)	0.6749 (7)	3.3 (2)
C(10)	0.959 (1)	0.2964 (8)	0.4635 (7)	3.6 (2)
O(1)	0.355 (1)	0.6283 (7)	0.1769 (6)	6.3 (2)
N(1)	0.3514 (9)	0.5833 (7)	-0.0102 (6)	4.1 (2)
C(11)	0.397 (1)	0.6462 (9)	0.0894 (8)	4.6 (2)
C(12)	0.411 (1)	0.611 (1)	-0.1104 (8)	5.4 (2)
C(13)	0.244 (1)	0.490 (1)	-0.026 (1)	6.1 (3)

* L(1-4) stands for the octahedral Re₆ cluster face-capping ligands, composed of L = 0.375 Cl + 0.625 S.

Table 2. Bond distances (Å) and angles (°) for (1) and (2) and hydrogen-bond geometry (Å, °) showing (1) over (2)

Dimer (1)			
Re(1)—Re(2)	2.590	S(1)—C(3)	1.747 (7)
Re(1)—Re(2) ⁱ	2.590	S(2)—C(1)	1.744 (6)
Re(1)—Re(3)	2.579	S(2)—C(4)	1.745 (7)
Re(1)—Re(3) ^j	2.593	S(3)—C(2)	1.706 (7)
Re(1)—Cl(1)	2.379 (2)	S(3)—C(5)	1.731 (7)
Re(1)—L(1)	2.432 (2)	S(4)—C(2)	1.741 (6)
Re(1)—L(2)	2.397 (2)	S(4)—C(6)	1.735 (7)
Re(1)—L(3) ^k	2.395 (1)	S(5)—C(7)	1.706 (8)
Re(1)—L(4)	2.423 (2)	S(5)—C(8)	1.683 (8)
Re(2)—Re(3) ^l	2.580	S(6)—C(9)	1.702 (7)
Re(2)—Re(3)	2.590	S(6)—C(10)	1.701 (7)
Re(2)—Cl(2)	2.368 (2)	C(1)—C(2)	1.396 (9)
Re(2)—L(1)	2.431 (2)	C(3)—C(4)	1.428 (9)
Re(2)—L(2) ^j	2.394 (2)	C(3)—C(7)	1.34 (1)
Re(2)—L(3)	2.412 (1)	C(4)—C(8)	1.37 (1)
Re(2)—L(4)	2.407 (2)	C(5)—C(6)	1.434 (8)
Re(3)—Cl(3)	2.375 (1)	C(5)—C(9)	1.349 (9)
Re(3)—L(1) ^j	2.416 (2)	C(6)—C(10)	1.37 (1)
Re(3)—L(2) ^j	2.411 (2)	O(1)—C(11)	1.21 (1)
Re(3)—L(3) ^j	2.413 (2)	N(1)—C(11)	1.31 (1)
Re(3)—L(4)	2.411 (2)	N(1)—C(12)	1.49 (1)
S(1)—C(1)	1.707 (6)	N(1)—C(13)	1.45 (1)
C(1)—S(1)—C(3)	95.9 (3)	C(4)—C(3)—C(7)	112.9 (6)
C(1)—S(2)—C(4)	94.2 (3)	S(2)—C(4)—C(3)	117.0 (5)
C(2)—S(3)—C(5)	95.6 (3)	S(2)—C(4)—C(8)	130.4 (6)
C(2)—S(4)—C(6)	93.9 (3)	C(3)—C(4)—C(8)	112.6 (7)
C(7)—S(5)—C(8)	93.9 (4)	S(3)—C(5)—C(6)	115.1 (5)
C(9)—S(6)—C(10)	93.3 (3)	S(3)—C(5)—C(9)	131.9 (5)
S(1)—C(1)—S(2)	118.0 (4)	C(6)—C(5)—C(9)	112.9 (6)
S(1)—C(1)—C(2)	122.8 (5)	S(4)—C(6)—C(5)	117.0 (5)
S(2)—C(1)—C(2)	119.2 (5)	S(4)—C(6)—C(10)	131.0 (5)
S(3)—C(2)—S(4)	118.1 (4)	C(5)—C(6)—C(10)	112.0 (6)
S(3)—C(2)—C(1)	121.1 (5)	S(5)—C(7)—C(3)	110.5 (6)
S(4)—C(2)—C(1)	120.7 (5)	S(5)—C(8)—C(4)	110.0 (6)
S(1)—C(3)—C(4)	114.9 (5)	S(6)—C(9)—C(5)	111.1 (5)
S(1)—C(3)—C(7)	132.1 (6)	S(6)—C(10)—C(6)	110.7 (5)
Dimer (2)			
Re(1)—Re(2)	2.589	S(1)—C(3)	1.743 (8)
Re(1)—Re(2) ⁱ	2.581	S(2)—C(1)	1.736 (7)
Re(1)—Re(3)	2.577	S(2)—C(4)	1.737 (9)
Re(1)—Re(3) ^j	2.589	S(3)—C(2)	1.724 (8)
Re(1)—Cl(1)	2.379 (2)	S(3)—C(5)	1.741 (8)
Re(1)—L(1)	2.428 (2)	S(4)—C(2)	1.730 (7)
Re(1)—L(2)	2.391 (2)	S(4)—C(6)	1.734 (9)
Re(1)—L(3) ^k	2.395 (2)	Se(1)—C(7)	1.823 (9)
Re(1)—L(4)	2.426 (2)	Se(1)—C(8)	1.83 (1)
Re(2)—Re(3) ^l	2.580	Se(2)—C(9)	1.851 (8)
Re(2)—Re(3)	2.585	Se(2)—C(10)	1.84 (1)
Re(2)—Cl(2)	2.362 (2)	C(1)—C(2)	1.36 (1)
Re(2)—L(1)	2.426 (2)	C(3)—C(4)	1.43 (1)
Re(2)—L(2) ^j	2.388 (2)	C(3)—L(7)	1.36 (1)
Re(2)—L(3)	2.401 (2)	C(4)—C(8)	1.34 (1)
Re(2)—L(4)	2.415 (2)	C(5)—C(6)	1.44 (1)
Re(3)—Cl(3)	2.373 (2)	C(5)—C(9)	1.35 (1)
Re(3)—L(1) ^j	2.406 (2)	C(6)—C(10)	1.37 (1)
Re(3)—L(2) ^j	2.411 (2)	O(1)—C(11)	1.22 (1)
Re(3)—L(3) ^j	2.411 (2)	N(1)—C(11)	1.34 (1)
Re(3)—L(4)	2.414 (2)	N(1)—C(12)	1.46 (1)
S(1)—C(1)	1.731 (8)	N(1)—C(13)	1.41 (1)
C(1)—S(1)—C(3)	95.1 (4)	C(4)—C(3)—C(7)	113.7 (7)
C(1)—S(2)—C(4)	96.1 (4)	S(2)—C(4)—C(3)	115.1 (6)
C(2)—S(3)—C(5)	96.1 (4)	S(2)—C(4)—C(8)	130.0 (7)
C(2)—S(4)—C(6)	95.1 (4)	C(3)—C(4)—C(8)	114.9 (8)
C(7)—S(5)—C(8)	88.1 (4)	S(3)—C(5)—C(6)	114.5 (6)
C(9)—S(6)—C(10)	89.1 (4)	S(3)—C(5)—C(9)	129.3 (6)
S(1)—C(1)—S(2)	116.8 (5)	C(6)—C(5)—C(9)	116.2 (7)
S(1)—C(1)—C(2)	122.1 (5)	S(4)—C(6)—C(5)	116.8 (6)
S(2)—C(1)—C(2)	121.0 (6)	S(4)—C(6)—C(10)	129.5 (6)
S(3)—C(2)—S(4)	117.1 (4)	C(5)—C(6)—C(10)	113.7 (8)
S(3)—C(2)—C(1)	120.0 (5)	Se(1)—C(7)—C(3)	111.6 (6)
S(4)—C(2)—C(1)	122.8 (6)	Se(1)—C(8)—C(4)	111.8 (7)
S(1)—C(3)—C(4)	116.9 (6)	Se(2)—C(9)—C(5)	110.1 (6)
S(1)—C(3)—C(7)	129.3 (6)	Se(2)—C(10)—C(6)	110.9 (6)
D—H...X			
	D...X	H...X	D—H...X
C(7)—H(7)...O(1) ⁱⁱ	3.24 (1)	2.62 (1)	123.0 (5)
	3.27 (1)	2.63 (1)	125.2 (6)
C(9)—H(9)...O(1) ⁱⁱⁱ	3.26 (1)	2.83 (1)	108.5 (5)
	3.21 (1)	2.82 (1)	105.6 (6)

Symmetry code: (i) -x, -y, -z; (ii) x, y, z; (iii) -x + 1, -y + 1, -z + 1.

1989; Desiraju, 1991). It is of interest to note that the achievement of a neat ordering of the DMF molecules in such cation radical solvates of large spherical inorganic anions tends to be associated, as in (BEDT-TTF)(Re₆Se₅Cl₉).(DMF)₂ (Pénicaud *et al.*, 1989), with the possibility for a centrosymmetrical DMF dimer to fit into the the solvate cavity. By

Table 3. *Intra and inter-dimer chalcogen...chalcogen distances (Å)*

(DT-TTF) ₂ Re ₆ S ₄ Cl ₆ (DMF) ₂		(DS-TTF) ₂ Re ₆ S ₄ Cl ₆ (DMF) ₂	
S(1)—S(3) ⁱ	3.272 (2)	S(1)—S(3) ⁱ	3.289 (3)
S(1)—S(6) ⁱⁱ	3.923 (3)	Se(2)—S(1) ⁱⁱ	3.882 (3)
S(2)—S(4) ⁱ	3.558 (2)	S(2)—S(4) ⁱ	3.545 (3)
S(4)—S(6) ⁱⁱ	3.672 (3)	Se(2)—S(4) ⁱⁱ	3.717 (2)
S(5)—S(5) ⁱⁱⁱ	3.942 (3)	Se(1)—Se(2) ⁱ	3.712 (1)
S(5)—S(6) ⁱⁱⁱ	3.642 (3)		

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$.

contrast, in the series of organic-inorganic solvates (BEDT-TTF)₄Re₆Se₃Cl₆(guest), where the neutral guest cavity size cannot accommodate two molecules of solvent, the incorporation of a non-centrosymmetrical molecule such as DMF results in a highly disordered structure (Pénicaud *et al.*, 1993).

The Re₆ chalcogenide cluster monoanion presents the expected geometry with averaged Re—Re, Re—L_i and Re—Cl_i bond distances of 2.587 (3) [2.584 (2)], 2.412 (4) [2.409 (4)] and 2.374 (4) Å [2.376 (6) Å], typical of this monoanion (Boubekour, 1989; Pénicaud *et al.*, 1993).

The DT-TTF and DS-TTF molecules are essentially planar and associated in strongly coupled, singly oxidized dimers, identified in Fig. 1 and characterized by a set of intra-dimer chalcogen...chalcogen contact distances (Table 3) much shorter than the corresponding S...S and Se...Se van der Waals separations [3.70 and 4.0 Å for (1) and (2), respectively]. The intra-dimer mode of overlap is totally eclipsed as seen in Fig. 1.

Single layers of organic cation radicals and inorganic cluster anions alternate along *c*. Remarkably, an organic donor slab develops by the association of the dimers along their long molecular axis direction (Fig. 2), an unprecedented pattern for any tetrathiafulvalene-based cation radical salt and a manifestation of the presence of exposed chalcogen atoms at the outskirts of the molecules. Indeed, such cation radical slabs are known to develop either by the association of coplanar donor molecules along their short molecular axis as in β-(BEDT-TTF)₂I₃ (Yagubskii, Schegolev, Laukhin, Komonovich, Kartsovnik, Zvarykina & Buravov, 1984), or by fitting mutually orthogonal dimers along both their short molecular axis direction and the normal to their molecular plane as in κ-(BEDT-TTF)₂Cu(NCS)₂ (Urayama, Yamochi, Saito, Nozawa, Sugano, Kinoshita, Sato, Oshima, Kawamoto & Tanaka, 1988). Two types of inter-dimer overlap mode are identified in (1) and (2) and shown for (1) in Fig. 1. These modes are such as to achieve an inter-dimer fitting pattern where the outer chalcogen atoms maximize their overlap, both between each other and with the inner S atoms of the TTF moieties. Hence, the two-dimensional network

of chalcogen...chalcogen intermolecular contacts summarized in Table 3 and shown in Fig. 2.

A single line with a Lorentzian shape and anisotropic characteristics is observed by ESR on a single crystal for both compounds. The ESR linewidth at 4.4 K varies between 4.8 and 5.3×10^{-4} T and 5.0 and 6.0×10^{-4} T for (1) and (2), respectively. A set of six measurements at room temperature of the *g* values at different orientations affords the determination of the *g* tensor eigenvalues $g_{\min} = 2.0018$ (2.0001), $g_{\text{int}} = 2.0058$ (2.0061) and $g_{\max} = 2.0110$ (2.0136) for (1) [(2)]. The g_{\min} value for the bis-(thiophene)-TTF, DT-TTF (1), is in fact close to the free electron value of 2.0023, as expected for a sulfur π-donor molecule where the *d* orbitals of the heteroatom do not contribute to the highest occupied molecular orbital (HOMO) of the cation radical (Terahara, Ohya-Nishiguchi, Hirota, Awaji, Kawase, Yoneda, Sugimoto & Yoshida, 1984). The g_{\min} value for the bis(selenophene)-TTF, DS-TTF, (2), is significantly smaller and almost reaches that ($g = 1.993$) of tetramethyltetraselenafulvalene, TMTSF (Kinoshita, Tokumoto, Anzai, Ishiguro, Saito, Yamabe & Teramae, 1984). In the latter, the significant correction of the free-electron *g* value reflects the strong spin-orbit coupling due to the contribution of the selenium *d* orbitals to the TMTSF HOMO. We conclude, on the basis of this small observed g_{\min} value, that there is a sizeable contribution from the *d* orbitals of the outer Se atom to the DS-TTF HOMO. Finally, the mixed-valence dimer spins are found to be essentially non-interacting as demonstrated by the fit of the spin susceptibility to a Curie-Weiss law with $\theta \approx -5$ K.

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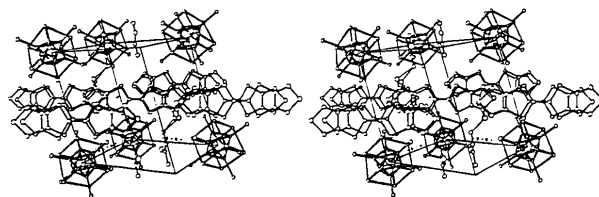


Fig. 1. Stereoview of the crystal structure of (1) looking down the normal to the cation radical molecular plane. The (C)H...O hydrogen bond is indicated by a thin line.

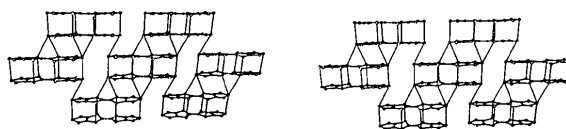


Fig. 2. A stereoview of the dimer slab in (1). The short S...S contacts (Table 4) are indicated by thinner lines.

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Structure of [FeH(N₂){(H₅C₂)₂PCH₂CH₂P(C₂H₅)₂}]₂BPh₄

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Abstract. Bis[1,2-bis(diethylphosphino)ethane-*P,P'*]-hydrido(dinitrogen-*N*)iron(II) tetraphenylborate, [FeH(N₂)(C₁₀H₂₄P₂)₂](C₂₄H₂₀B), *M_r* = 816.6, monoclinic, *P*2₁/*n*, *a* = 16.493 (3), *b* = 13.691 (4), *c* = 21.422 (8) Å, β = 111.20 (2)°, *V* = 4509.8 Å³, *Z* = 4, *D_x* = 1.203 Mg m⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 0.503 mm⁻¹, *F*(000) = 1752, *T* = 293 K, *R* = 0.0651 for 5651 independent observed reflections. The title compound was prepared in 86% yield from [FeHCl{(H₅C₂)₂PCH₂CH₂P(C₂H₅)₂}]₂ and NaBPh₄ in methanol under an atmosphere of nitrogen. The molecule consists of hydride *trans* to 'end-bound' molecular nitrogen and two bisphosphine ligands in a pseudo-octahedral arrangement about the iron centre.

Introduction. Complexes with molecular nitrogen bound to transition metals are important models for the active sites in nitrogenase enzymes (Chatt, Dilworth & Richards, 1978; Eady, 1991; Leigh, Prieto-Alcon & Sanders, 1991). Since this enzyme is known to feature an active site which incorporates an iron centre, complexes of iron bound to molecular nitrogen are of particular interest. Although several

iron hydrido-dinitrogen species are known, only [FeH(N₂)(P₄)]⁺ (P₄ = hexaphenyl-1,4,7,10-tetraphosphadecane) and [FeH₂(N₂)(PEtPh₂)₃] (Ghilardi, Midollini, Sacconi & Stoppioni, 1981; Van der Sluys *et al.*, 1990) have been fully structurally characterized, while recently a brief communication on the structure of [FeH(N₂)(dmpe)₂]⁺ [dmpe = 1,2-bis-(dimethylphosphino)ethane] was published (Hills, Hughes, Jimenez-Tenorio & Leigh, 1990). An analogue of the latter complex, [FeH(N₂)(depe)₂]-BPh₄ [depe = 1,2-bis(diethylphosphino)ethane], was one of the earliest literature examples of a molecular nitrogen adduct (Bancroft, Mays & Prater, 1969). We have been studying the reactions of [FeH(N₂)(depe)₂]⁺ as part of our continuing investigations on transition-metal complexes involving bisphosphine ligands. During this research we obtained crystals of suitable quality for diffraction studies and we now report in detail the structure of the title complex.

Experimental. [FeH(N₂)(depe)₂]-BPh₄ was prepared by a modified literature method (Bancroft *et al.*, 1969). Under a nitrogen atmosphere, 0.18 g (0.29 mmol) [FeHCl(depe)₂] was dissolved in 10 cm³ of methanol. Addition of 0.98 g (0.29 mmol) NaBPh₄ gave [FeH(N₂)(depe)₂]-BPh₄ in 86% yield as a buff-

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