Fig. 2. Vue stéréo de la molécule.

d'autres composés organosiliciés. Les distances Si—C varient de 1,825 à 1,919 Å (moyenne de 1,870 Å) avec des angles C—Si—C compris entre 105 et 116° (moyenne de 109,5°). On peut remarquer un allongement de la distance C(10)—C(11) dû probablement à l'encombrement stérique des groupements triméthylsilyles portés par chacun de ces carbones. Les angles dièdres calculés sur les substituants des carbones C(10) et C(11) montrent que les groupes triméthylsilyles sont situés de part et d'autre du cycle benzénique (Fig. 2). Ce dernier est plan avec les atomes C(10) et O(12) situés dans le plan alors que le silicium Si(14) s'en écarte légèrement [δSi(14) = + 0,06 Å].

Le cycle benzénique présente un léger pincement le long de l'axe 1–4 [angles correspondants de 116,1 (2) et 116,2 (2)°] entraînant une augmentation de la valeur des autres angles du cycle.

L'absence d'atomes donneurs et accepteurs dans la molécule entraîne de très faibles contacts intramoléculaires. Les distances intramoléculaires les plus courtes sont:

C(53)	$(x, y, z) \cdots C(53)$	$(-x, 1-y, -z)$	3,734 (6) Å
C(3)	$(x, y, z) \cdots C(72)$	$(1-x, -y, 1-z)$	3,782 (5) Å
C(51)	$(x, y, z) \cdots C(74)$	$(1-x, -y, 1-z)$	3,867 (6) Å
C(72)	$(x, y, z) \cdots C(72)$	$(1-x, -y, 1-z)$	3,857 (6) Å.

Ces très faibles contacts intramoléculaires expliquent probablement la très faible densité de ce composé ainsi que son très bas point de fusion: $T_f = 363$ K.

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Structure of Bis(2,2',5,5'-tetrathiafulvalenium)* Dodeca-μ-chloro-*octahedro*-hexakis(chlorotantalate) Diacetonitrile Solvate

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Abstract. $[C_6H_4S_4]_2[Ta_6Cl_{18}].2C_2H_3N$, $M_r = 2214.66$, triclinic, $P\bar{1}$, $a = 8.633$ (6), $b = 10.405$ (5), $c = 12.942$ (8) Å, $\alpha = 93.42$ (4), $\beta = 99.00$ (4), $\gamma = 91.72$ (4)°, $V = 1145.2$ Å³, $Z = 1$, $D_x = 3.21$ g cm⁻³, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 155.47$ cm⁻¹, $F(000) = 996$, room temperature, $R = 0.070$ based on 3587 unique observed reflections. The organic radical cations are dimerized and form with the inorganic anions a distorted cubic coordination typical of the CsCl-type of structure. The centrosymmetrically related organic ions

* Bis(2,2'-bi-1,3-dithiolylidenium).

$(TTF^+)_2$ are eclipsed. This unusual configuration, which maximizes the sulfur–sulfur interaction, results in a short intradimer S$\cdots$S distance of 3.395 (6) Å.

Introduction. Hybrid salts of organic donors such as tetrathiafulvalene (TTF) and its substituted derivatives have recently been reported with the all-inorganic octahedral metal-cluster anions $|(Mo_6Cl_8)Cl_6|^{2-}$ (Ouahab, 1985; Ouahab, Batail, Perrin & Garrigou-Lagrange, 1986), $[(Re_6Se_5Cl_3)Cl_6]^-$ (Batail, Ouahab, Penicaud, Lenoir & Perrin, 1987) and $|(Nb_6Cl_{12})Cl_6|^3$ (Penicaud, Batail, Perrin, Coulon, Parkin & Torrance, 1987). In the course of our investigations on this class of organomineral material, we have prepared new salts with the tantalum anions $|(Ta_6Cl_{12})Cl_6|^{n-}$. We report here the structure of $(TTF)_2Ta_6Cl_{18}(CH_3CN)_2$.

Experimental. The compound was prepared by the electrocrystallization technique from the neutral donor in a rigorously dried mixture of acetonitrile (85%) and dichloromethane (15%), using tetraethylammonium salts of the anion. The electrocrystallization was carried out under constant low current (0.9 μA) in a 50 ml cell with two glass frits as separators. The working electrode was a platinum wire.

Crystal 0.09 × 0.08 × 0.07 mm. Enraf–Nonius CAD-4 diffractometer, graphite-crystal-monochromatized Mo $K\alpha$ radiation. Cell dimensions: least-squares refinement from setting angles of 25 accurately centered reflections ($\theta < 16°$). Intensities collected by θ–2θ scans. Three standard reflections measured every hour: no fluctuations in intensity. One set of reflections collected up to $2\theta = 50°$. 4431 independent reflections measured ($-10 \le h \le 10$, $-12 \le k \le 12$, $0 \le l \le 15$), 3587 with $I > 3\sigma(I)$. Lorentz and polarization corrections, no absorption correction. Direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). H atoms placed at geometrically reasonable positions. Full-matrix least-squares anisotropic (β_{ij}) refinement (H atoms isotropic, not refined), $R = 0.070$, $wR = 0.089$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/[\sigma^2(|F_o|) + (0.07F_o)^2]$, $S = 2.28$, $(\Delta/\sigma)_{max} = 0.04$, $\Delta\rho_{max} = |2.6| e \text{ Å}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). All computer programs from Enraf–Nonius *SDP* described by Frenz (1978).

Discussion. Final atomic parameters are in Table 1,* bond distances and angles in Table 2. The atomic numbering is shown in Fig. 1.

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51181 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ta1	0.10682 (7)	−0.12239 (6)	−0.10107 (4)	1.32 (1)
Ta2	0.16908 (7)	−0.04403 (6)	0.12755 (4)	1.32 (1)
Ta3	0.14500 (7)	0.15690 (6)	−0.02891 (4)	1.30 (1)
Cl1	0.3153 (4)	−0.1908 (4)	0.0303 (3)	1.98 (7)
Cl2	0.2894 (4)	0.0386 (4)	−0.1491 (3)	2.03 (7)
Cl3	0.3606 (4)	0.1248 (4)	0.1099 (3)	1.92 (7)
Cl4	−0.0417 (5)	−0.3195 (4)	−0.0817 (3)	2.24 (7)
Cl5	−0.0710 (5)	−0.0916 (4)	−0.2612 (3)	2.22 (7)
Cl6	−0.251 (5)	0.2284 (4)	−0.1805 (3)	2.17 (7)
Cl7	0.2347 (5)	−0.2673 (4)	−0.2204 (3)	2.66 (8)
Cl8	0.3690 (5)	−0.0959 (4)	0.2788 (3)	2.77 (8)
Cl9	0.3153 (5)	0.3433 (4)	−0.0606 (3)	2.40 (7)
S1	0.4377 (6)	0.3419 (4)	0.3207 (3)	2.76 (9)
S2	0.2602 (6)	0.5731 (5)	0.3370 (4)	3.4 (1)
S3	0.2140 (6)	0.5089 (4)	0.5724 (4)	2.65 (8)
S4	0.3894 (6)	0.2772 (4)	0.5540 (4)	2.85 (9)
C1	0.328 (2)	0.437 (2)	0.395 (1)	2.3 (3)
C2	0.417 (2)	0.435 (2)	0.217 (1)	3.1 (4)
C3	0.338 (2)	0.543 (2)	0.223 (1)	2.7 (3)
C4	0.310 (2)	0.409 (2)	0.495 (1)	2.4 (3)
C5	0.245 (3)	0.413 (2)	0.678 (1)	3.4 (4)
C6	0.322 (2)	0.309 (2)	0.670 (1)	2.8 (3)
N	0.019 (3)	0.788 (3)	0.474 (3)	8.8 (8)
C7	0.124 (3)	0.854 (3)	0.505 (2)	5.2 (6)
C8	0.263 (3)	0.931 (2)	0.549 (2)	4.7 (5)

The crystal structure represented in Fig. 2(*a*) is built from the $|Ta_6Cl_{18}|^{2-}$ units located at the origin and the dimerized organic radical cation lying at the center of the unit cell. In addition, two solvent molecules (CH_3CN) are located in channels running parallel to the |100| direction.

A comparison of the structural features of the $|Ta_6Cl_{18}|^{2-}$ moiety with those of $H_2|Ta_6Cl_{18}|.6H_2O$ (Thaxton & Jacobson, 1971), another compound containing the $|Ta_6Cl_{18}|^{2-}$ unit whose structure has been determined, shows good similarity in bond distances. In contrast, the Ta–Ta distances would be shorter in the case of $|Ta_6Cl_{18}|^{3-}$ and $|Ta_6Cl_{18}|^{4-}$ units (Brničević, Ružic-Toroš, Kojić-Prodić, 1985).

In the organic molecule, the bond lengths C(1)–C(4) = 1.38 (3) Å of the central ethylenic part, as well as C(1)–S(1,2) and C(4)–S(3,4) |1.72 (2) Å|, are identical to corresponding distances in fully oxidized TTF salts such as $(TTF)X$ (X = Cl, Br) (Scott, La Placa, Torrance, Silverman & Welber, 1977) and $(TTF)I_3$ (Teitelbaum, Marks & Johnson, 1980). The 2:1 stoichiometry also suggests fully oxidized organic molecules in agreement with the insulating character of this material: the organic molecules form fully oxidized dimers, which act as large divalent cations. The dimers are interspersed [with an interdimer S$\cdots$S distance of 5.765 (8) Å| with metal cluster anions of opposite charge in a distorted cubic coordination (Fig. 2) typical of the CsCl structural type: this structure is then closely related to that of $(TMTTF)_2Mo_6Cl_{14}$ where the cluster unit is undoubtedly divalent (Ouahab, Batail, Perrin & Garrigou-Lagrange, 1986). The intradimer interaction
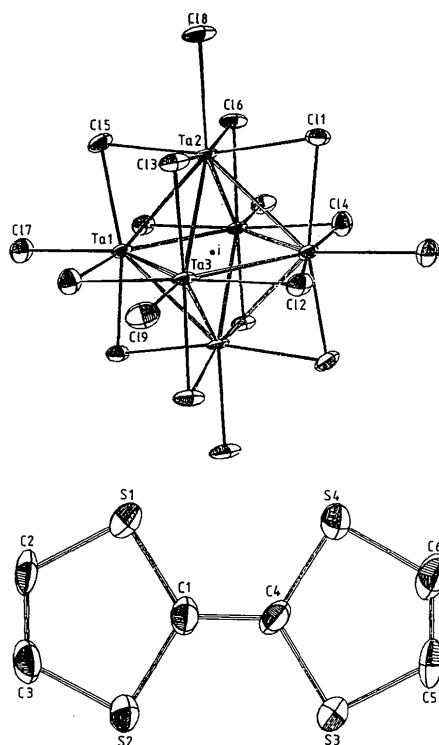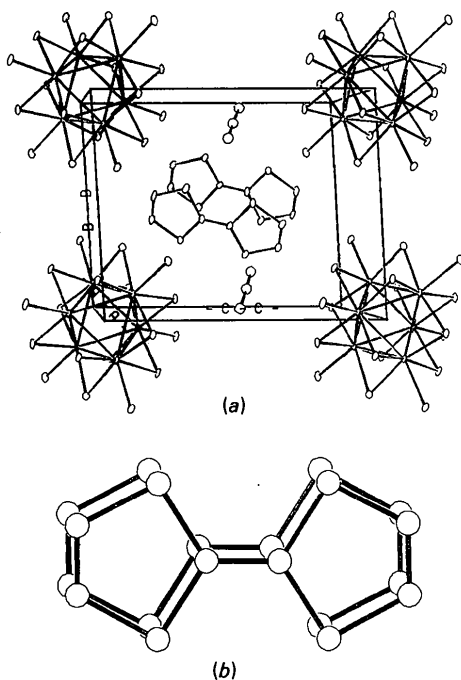
Fig. 1. Atom numbering.

(a)

(b)

Fig. 2. (a) Perspective view of the structure along the c axis. (b) Eclipsed intradimer evidence.

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

Ta1—Ta2	2·983 (1)	Ta3—Cl9	2·491 (4)
Ta1—Ta3	2·991 (1)	S1—C1	1·73 (2)
Ta1—Cl1	2·429 (4)	S1—C2	1·70 (2)
Ta1—Cl2	2·439 (4)	S2—C1	1·72 (2)
Ta1—Cl4	2·433 (4)	S2—C3	1·73 (2)
Ta1—Cl5	2·423 (4)	S3—C4	1·72 (2)
Ta1—Cl7	2·497 (5)	S3—C5	1·73 (2)
Ta2—Ta3	2·986 (1)	S4—C4	1·72 (2)
Ta2—Cl1	2·428 (4)	S4—C6	1·72 (2)
Ta2—Cl3	2·422 (4)	C1—C4	1·38 (3)
Ta2—Cl8	2·495 (4)	C3—C2	1·33 (3)
Ta3—Cl2	2·441 (4)	C5—C6	1·30 (3)
Ta3—Cl3	2·422 (4)	N—C7	1·13 (4)
Ta3—Cl6	2·428 (4)	C7—C8	1·44 (4)

Ta2—Ta1—Ta3	59·97 (2)	Ta1—Ta3—Cl2	52·17 (9)
Ta2—Ta1—Cl1	52·09 (9)	Ta1—Ta3—Cl3	94·00 (9)
Ta2—Ta1—Cl2	95·02 (9)	Ta1—Ta3—Cl6	94·59 (9)
Ta2—Ta1—Cl4	95·0 (1)	Ta1—Ta3—Cl9	136·0 (1)
Ta2—Ta1—Cl5	142·5 (1)	Ta2—Ta3—Cl2	94·90 (9)
Ta2—Ta1—Cl7	134·8 (1)	Ta2—Ta3—Cl3	51·95 (9)
Ta3—Ta1—Cl1	95·08 (9)	Ta2—Ta3—Cl6	142·3 (1)
Ta3—Ta1—Cl2	52·23 (9)	Ta2—Ta3—Cl9	134·77 (9)
Ta3—Ta1—Cl4	142·5 (1)	Cl2—Ta3—Cl3	87·9 (1)
Ta3—Ta1—Cl5	95·6 (1)	Cl2—Ta3—Cl6	88·3 (1)
Ta3—Ta1—Cl7	134·9 (1)	Cl2—Ta3—Cl9	83·8 (1)
Cl1—Ta1—Cl2	89·1 (1)	Cl3—Ta3—Cl6	165·6 (1)
Cl1—Ta1—Cl4	88·5 (1)	Cl3—Ta3—Cl9	82·9 (1)
Cl1—Ta1—Cl5	165·4 (1)	Cl6—Ta3—Cl9	82·9 (1)
Cl1—Ta1—Cl7	82·7 (1)	Ta1—Cl1—Ta2	75·8 (1)
Cl2—Ta1—Cl4	165·3 (1)	Ta1—Cl2—Ta3	75·6 (1)
Cl2—Ta1—Cl5	89·5 (1)	Ta2—Cl3—Ta3	76·1 (1)
Cl2—Ta1—Cl7	82·7 (1)	C1—S1—C2	95·4 (9)
Cl4—Ta1—Cl5	89·1 (1)	C1—S2—C3	95·4 (9)
Cl4—Ta1—Cl7	82·6 (1)	C4—S3—C5	93·8 (9)
Cl5—Ta1—Cl7	82·6 (1)	C4—S4—C6	95·4 (9)
Ta1—Ta2—Ta3	60·16 (2)	S1—C1—S2	115 (1)
Ta1—Ta2—Cl1	52·14 (8)	S1—C1—C4	122 (1)
Ta1—Ta2—Cl3	94·21 (9)	S2—C1—C4	124 (1)
Ta1—Ta2—Cl8	135·2 (1)	S2—C3—C2	116 (1)
Ta3—Ta2—Cl1	95·3 (1)	S3—C4—S4	115 (1)
Ta3—Ta2—Cl3	51·95 (9)	S3—C4—C1	122 (1)
Ta3—Ta2—Cl8	134·9 (1)	S4—C4—C1	123 (1)
Cl1—Ta2—Cl3	88·2 (1)	S3—C5—C6	119 (2)
Cl1—Ta2—Cl8	83·1 (1)	S4—C6—C5	117 (2)
Cl3—Ta2—Cl8	83·0 (1)	S1—C2—C3	118 (2)
Ta1—Ta3—Ta2	59·87 (2)	N—C7—C8	176 (3)

occurs through the sulfur p-orbitals overlap since the centrosymmetrically related ions in (TTF⁺)₂ are eclipsed (Fig. 2b), an unusual configuration which maximizes the sulfur–sulfur bonding (Lowe, 1980). This results in short intradimer S···S distances of 3·395 (6) and 3·418 (7) Å for S1···S3 and S2···S4, respectively.

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Amine(salicylaldehyde thiosemicarbazonato)nickel(II)

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Abstract. $[Ni(C_8H_7N_3OS)(NH_3)]$, $M_r = 268\cdot96$, monoclinic, $P2_1/c$, $a = 4\cdot768$ (2), $b = 18\cdot289$ (5), $c = 12\cdot025$ (3) Å, $\beta = 105\cdot75$ (4)°, $V = 1009\cdot2$ (6) Å³, $Z = 4$, $D_m = 1\cdot78$ (2), $D_x = 1\cdot77$ g cm⁻³, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 20\cdot9$ cm⁻¹, $F(000) = 552$, room temperature, $R = 0\cdot042$ for 1296 observed reflections. A molecule of salicylaldehyde thiosemicarbazone coordinates in a planar conformation to the central Ni atom through O, N and S atoms, interatomic distances being Ni—O = 1·844 (4), Ni—N = 1·856 (4) and Ni—S = 2·139 (2) Å. A fourth coordination site is occupied by the ammonia molecule, Ni—N = 1·919 (4) Å.

Introduction. The complex of nickel(II) with salicylaldehyde thiosemicarbazone forms two isomers differing by the unit-cell parameters and apparently by the packing of the molecules. The results of elemental analysis and IR spectrometry indicate that the two isomers are chemically identical (Gyepes, Pavelčik & Beňo, 1981). The main goal of this work was to determine the crystal and molecular structure of the complex because of its analytical importance. Salicylaldehyde thiosemicarbazonates are widely used in analytical practice, *e.g.* for the gravimetric determination of Cd^{II}, spectrophotometric determination of Mn^{II} and separation of Mn^{II} and Ni^{II} by extraction (Holzbecher, 1972).

Experimental. Red-brown prismatic crystals with roughly hexagonal cross-section prepared by hot-mixing of equimolar methanolic solutions of salicylaldehyde thiosemicarbazone and nickel(II) nitrate in the presence of ammonia. Crystal dimensions approxi-

mately $0\cdot01 \times 0\cdot02 \times 0\cdot04$ cm, D_m by flotation (thallous formate–malonate–water). Syntex $P2_1$ diffractometer, 15 reflections for lattice-parameter determination, $18 < 2\theta < 30°$, absorption ignored, $2\theta_{max} = 55°$, *hkl* range $0,0,\overline{14}$ to $5,21,13$. Two standard reflections measured every 100 reflections showed no significant changes during intensity-data collection. 1788 reflections measured, 1296 of them observed with $I > 2\cdot5\sigma(I)$. Ni-atom position found from Patterson map, other non-H atoms located from successive Fourier maps. H atoms from difference Fourier map and geometry. Full-matrix refinement of 45 positional parameters, 90 anisotropic thermal parameters and one overall scale factor for non-H atoms, H atoms not refined. Refinement based on F, $R = 0\cdot042$, $wR = 0\cdot038$, $S = 0\cdot51$, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{max} = 0\cdot2$ in final refinement cycle for non-H atoms, $\Delta\rho$ in final difference Fourier synthesis $|0\cdot4|$ e Å⁻³. All calculations performed at the Department of Crystal Structures, Institute of Chemistry, University of Wrocław on a Nova 1200 computer, *XTL* system (Syntex, 1973), atomic scattering factors from *International Tables for X-ray Crystallography* (1968).

Discussion. Final positional and equivalent isotropic thermal parameters of the non-H atoms are listed in Table 1,* interatomic distances and bond angles in

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