

First Cation Radical Mixed-valence Hybrid Salts of the Paramagnetic Octahedral Cluster $\text{Nb}_6\text{Cl}_{18}^{3-}$. Preparation, Crystal Structures, and Conducting and Magnetic Properties of Pentakis(2,3,6,7-tetramethyl-1,4,5,8-tetra-selena- and -thia-fulvalenium) Hexachloro(dodeca- μ_2 -chloro-octahedro-hexaniobate)

Alain Penicaud,^a Patrick Batail,^{*a} Christiane Perrin,^b Claude Coulon,^c Stuart S. P. Parkin,^d and Jerry B. Torrance^d

^a *Laboratoire de Physique des Solides Associé au CNRS, Université de Paris-Sud, 91405 Orsay, France*

^b *Laboratoire de Chimie du Solide et Inorganique Moléculaire Associé au CNRS, Université de Rennes I, 35042 Rennes, France*

^c *Centre de Recherche Paul Pascal, Domaine Universitaire de Bordeaux I, 33405 Talence*

^d *IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, U.S.A.*

Electrically conducting single crystals of $(\text{D})_5\text{Nb}_6\text{Cl}_{18}(\text{CH}_2\text{Cl}_2)_{0.5}$ [$\text{D} = 2,3,6,7$ -tetramethyl-1,4,5,8-tetra-selena- and -thia-fulvalene (TMTSF) and (TMTTF) in (1) and (2) respectively] have been grown electrochemically; their unique crystal structure shows a one-dimensional stack with a periodicity twice that of the Bechgaard salts; the observed Curie-Weiss behaviour of the magnetic susceptibility demonstrates the presence of one non-interacting spin per unit-cell; this is not purely a cluster spin as indicated by e.s.r. spectroscopy.

Hybrid salts of organic donors such as tetrathiafulvalenium and a variety of its substituted derivatives have recently been prepared with the isostructural and isoelectronic all-inorganic octahedral metal cluster anions $\text{Mo}_6\text{Cl}_8(\text{Cl}_6)^{2-}$ and $\text{Re}_6\text{Se}_5\text{Cl}_3(\text{Cl}_6)^{-}$.^{1,2} It was found that changing the charge of the anion resulted in profound modifications of the structure and conducting and magnetic properties of the salts. This prompted us to prepare similar combinations with the larger paramagnetic niobium halide cluster anion,³ $\text{Nb}_6\text{Cl}_{12}(\text{Cl}_6)^{3-}$. The electrochemical preparation and unique crystal structure

and conducting and magnetic properties of such hitherto unknown hybrids are reported here.

Black needle-like single-crystals of the solvates $(\text{D})_5\text{Nb}_6\text{Cl}_{18}(\text{CH}_2\text{Cl}_2)_{0.5}$ [$\text{D} = 2,3,6,7$ -tetramethyl-1,4,5,8-tetra-selena- and -thia-fulvalene (TMTSF) and (TMTTF) in (1) and (2), respectively] were grown at a platinum wire anode by constant current electrolysis ($J = 1 \mu\text{A cm}^{-2}$) of a $\text{MeCN}-\text{CH}_2\text{Cl}_2$ (4:1) mixture containing the donor (10^{-3} M) and $[\text{Et}_4\text{N}]_3\text{Nb}_6\text{Cl}_{18}^4$ ($2 \times 10^{-3} \text{ M}$). The stoichiometry was determined by resolution of the crystal structure.

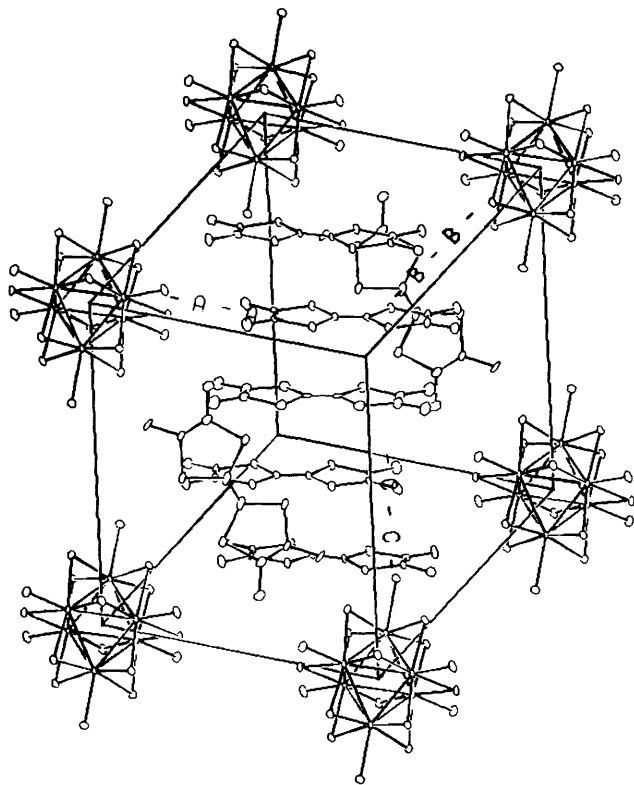


Figure 1. A view of the unit-cell. Two clusters at corners of the unit-cell have been omitted for clarity.

Unit-cell parameters for compounds (1) and (2) are similar. A single-crystal X-ray structure determination has so far been carried out on (1) only.[†] The crystal structure (Figure 1) is composed of stacks of TMTSF molecules parallel to the needle axis *c*, surrounded by $\text{Nb}_6\text{Cl}_{18}^{3-}$ clusters at the origin of the cell and additional TMTSF molecules orthogonal to the stacks and located on the (010) plane. In addition, a disordered solvent molecule was detected in a cavity centred at the middle of the (100) plane. The average values of the two sets of intracuster Nb–Nb distances [2.995(1) and 3.007(1) Å] are intermediate between those [2.967(5) and 3.018(2) Å] found³ for the

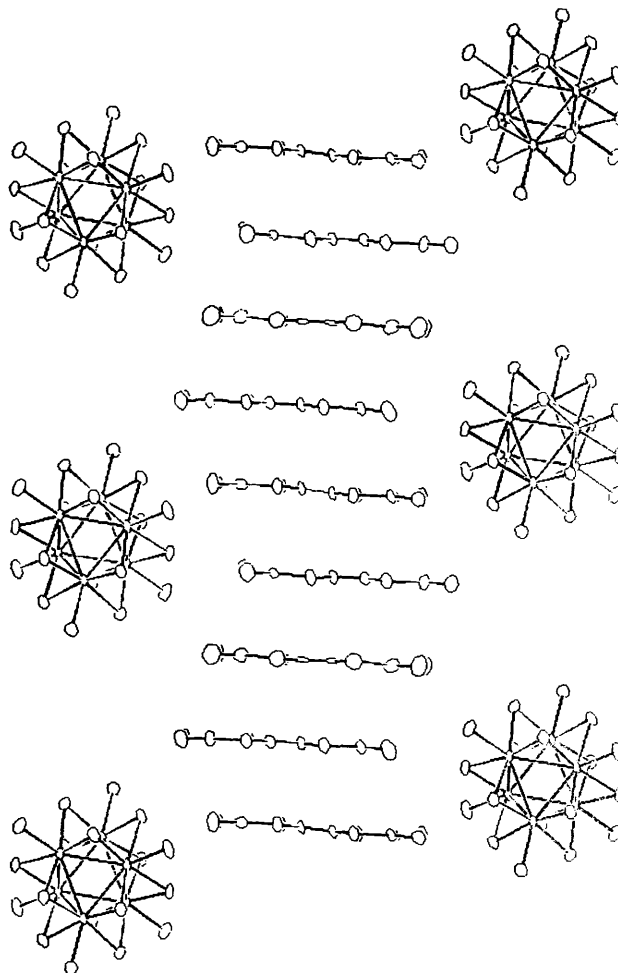


Figure 2. Side-view of the stack.

ammonium salts of $\text{Nb}_6\text{Cl}_{18}^{m-}$ ($m = 3, 2$), with a formal cluster electron count of 15 and 14, respectively. The clusters are loosely packed since the shortest distance between their centres ($a = 13.17$ Å) is somewhat larger than those found in $[\text{Me}_4\text{N}]_3\text{Nb}_6\text{Cl}_{18}$ ⁵ and $\text{LuNb}_6\text{Cl}_{18}$ ⁶ (11.40 and 9.22 Å, respectively). This strongly suggests that the organic stack determines the structure. Indeed, the stacks accommodate the large trivalent anions by both a larger spacing (every 4 cations instead of 2) and a bigger amplitude of the usual zig-zag mode of overlapping (Figure 2) than in the classical series $(\text{TMTSF})_2\text{X}$ with smaller monovalent inorganic anions.⁷ Hence, this unprecedented arrangement leads to a doubling of the latter stacking axis (14.581 vs. 7.266–7.299 Å). Since the organic stack is generated by two half-molecules located on centres of symmetry and one in a general position, two independent sets of intrastack Se ··· Se contacts between consecutive molecules are observed. Small differences in these contacts (3.88–3.98 Å vs. 3.74–3.85 Å) which are slightly shorter than those observed⁷ in the Bechgaard salts, suggest we may regard the stack as comprising groups of three TMTSF molecules separated by a single molecule. The observed activated [$E_g = 0.17$ and 0.20 eV for (1) and (2)] electrical conductivities, $0.5 \Omega^{-1} \text{ cm}^{-1}$ for (1) at room temperature (four-probe measurements along the needle axis of the crystal), are consistent with a non-integral oxidation state of the molecules along the stack.

[†] Crystal data for (1): $\text{C}_{50}\text{H}_{60}\text{Cl}_{18}\text{Nb}_6\text{Se}_{20} \cdot 0.5(\text{CH}_2\text{Cl}_2)$, $M = 3478.29$, triclinic, space group $P\bar{1}$, $a = 13.1762(6)$, $b = 13.8467(6)$, $c = 14.5812(6)$ Å, $\alpha = 113.79(3)$, $\beta = 96.47(3)$, $\gamma = 99.94(3)^\circ$, $U = 2348.1$ Å³, $D_{\text{calc.}} = 2.46 \text{ g cm}^{-3}$, $Z = 1$, $\mu(\text{Mo-K}\alpha) = 89.05 \text{ cm}^{-1}$; (2): $\text{C}_{50}\text{H}_{60}\text{Cl}_{18}\text{Nb}_6\text{S}_{20} \cdot 0.5(\text{CH}_2\text{Cl}_2)$, $M = 2540.37$, space group $P\bar{1}$, $a = 12.942(2)$, $b = 13.682(1)$, $c = 14.353(2)$ Å; $\alpha = 114.42(1)$, $\beta = 97.03(1)$, $\gamma = 9.18(1)^\circ$, $U = 2233.84$ Å³, $D_{\text{calc.}} = 1.89 \text{ g cm}^{-3}$, $Z = 1$. X-Ray diffraction data were collected for (1) on an Enraf–Nonius CAD4-PDP 1170 diffractometer system using a ω - 2θ scan technique with graphite-monochromated Mo– $K\alpha$ radiation. A total of 7850 independent reflexions were measured (to $\theta = 50^\circ$), of which 5154 were judged to be ‘observed’ [$I > 3\sigma(I)$]. The structure was solved by a combination of conventional heavy-atom and direct methods and least-squares refinement reached $R = 0.070$ ($R_w = 0.086$). The methyl hydrogen atoms were included in fixed calculated positions. The carbon and chlorine atoms (C26, Cl10, Cl11) of the solvent molecule were included in fixed observed positions. Refinement of their occupancy factors converged to 0.25. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The temperature dependence of the magnetic susceptibility (measured directly on single crystals using a SQUID magnetometer) presents a Curie-like behaviour and indicates the presence of one non-interacting ($S = 1/2$) spin per unit-cell for both compounds. Preliminary room-temperature single-crystal e.s.r. measurements reveal a single line with anisotropic characteristics for (1) [$g = 1.979; 1.976; 1.963$, $\Delta H = 90; 65; 60$ G ($1 \text{ G} = 10^{-4} \text{ T}$), respectively] and a narrower quasi-isotropic single line for (2) ($g = 1.982$, $\Delta H = 17$ G). These values are intermediate between those expected for a purely organic spin⁸ ($g = 2.002$ and $\Delta H = 3$ G) and those measured[‡] for the isolated paramagnetic cluster ion in $[\text{Et}_4\text{N}]_3\text{Nb}_6\text{Cl}_{18}$ ($g = 1.9577$ and $\Delta H = 115$ G). This suggests that a mixing of the electronic states of the donors and of the metal clusters might occur at room temperature, possibly related to (i) the observation of a strong $\text{Se} \cdots \text{Cl}$ interaction (3.368 \AA compared to a van der Waals separation of 3.70 \AA) between the independent TMTSF molecule in the stack and the cluster; (ii) the observed metal-metal distances in the Nb_6

octahedra consistent with an intermediate electron count on the cluster.

Received, 18th September 1986; Com. 1339

References

- 1 P. Batail and L. Ouahab, *Mol. Cryst. Liq. Cryst.*, 1985, **125**, 205; L. Ouahab, P. Batail, C. Perrin, and C. Garrigou-Lagrange, *Mater. Res. Bull.*, 1986, **21**, 1223.
- 2 P. Batail, L. Ouahab, A. Penicaud, C. Lenoir, and A. Perrin, *C. R. Acad. Sci.*, 1986, submitted.
- 3 R. E. McCarley, 'Mixed-Valence Compounds,' ed. D. B. Brown, D. Reidel, Dordrecht, Holland, 1979, p. 351.
- 4 For the preparation of the ammonium salt of this cluster, see: (a) R. A. McKay and R. F. Schneider, *Inorg. Chem.*, 1967, **6**, 549; (b) F. W. Koknat, J. A. Parson, and A. Vongvusharintra, *ibid.*, 1974, **13**, 7.
- 5 F. W. Koknat and R. E. McCarley, *Inorg. Chem.*, 1974, **13**, 295.
- 6 S. Ihmaine, C. Perrin, and M. Sergent, *C. R. Acad. Sci., Ser. II*, 1986, **303**, 1293.
- 7 N. Thorup, G. Rindorf, H. Soling, and K. Bechgaard, *Acta Crystallogr., Sect. B*, 1981, **37**, 1236.
- 8 H. J. Pedersen, J. C. Scott, and K. Bechgaard, *Solid State Commun.*, 1980, **35**, 207.

‡ Note that while this g value agrees well with that previously reported,^{4a} our observed ΔH value is about ten times smaller.