

Tetrathiafulvalene–FePS₃ Layered Intercalation Compound: A New Type of Organic–Inorganic Metal

Leticia Lomas, Pascal Lacroix, Jean Paul Audière and René Clément*

Laboratoire de Chimie Inorganique, C.N.R.S. U.R.A. 420, Université Paris Sud, 91405 Orsay Cedex, France

Layered FePS₃ preintercalated with tetraethylammonium cations reacts with (TTF)₃(BF₄)₂ in acetonitrile to yield Fe_{1-x}PS₃(TTF)_{2x} ($x \approx 0.18$). This intercalation compound has a metallic character, in contrast to pure FePS₃ which is a semiconductor.

Keywords: Layered material; Intercalation; Molecular metal

The MPS₃ layered materials, where M is a transition metal in the 2+ oxidation state, give rise to unusual intercalation chemistry based on the ability of the MPS₃ slabs to lose a variable amount of M²⁺ intralayer cations.^{1,2} This provides an opportunity to build up air-stable composites having original properties with respect to the parent compounds, such as the ferromagnetic intercalates with high Curie temperatures recently described.³ Intercalation of tetrathiafulvalene (TTF) monocations by ion exchange has already been achieved in two MPS₃ phases (M = Mn, Cd),⁴ in contrast to the redox processes involved in the previously developed intercalation chemistry of TTF into FeOCl, silicates and V₂O₅.^{5–9} This communication shows that insertion of TTF⁺ cations into FePS₃ leads to an intercalation compound which exhibits electrical properties drastically different from those of the pure host material.

Pure FePS₃ was synthesized by reaction of the elements at 730 °C.¹⁰ Intercalation was carried out in two steps. A sample of the tetraethylammonium intercalate Fe_{1-x}PS₃(Et₄N)_{2x}(soln)_y ($x \approx 0.14$) was obtained by treating FePS₃ (2 days at 50 °C) with a large excess of an aqueous solution containing Et₄NCl (*ca.* 1 mol dm⁻³) and EDTA (*ca.* 0.02 mol dm⁻³) at *ca.* pH 10 fixed by a Na₂CO₃/NaHCO₃ buffer. Insertion of TTF monocations was then achieved by treating the above intercalate (*ca.* 200 mg) with a solution of *ca.* 200 mg of (TTF)₃(BF₄)₂¹¹ in dry acetonitrile (*ca.* 20 cm³) for 2 days at 50 °C. The black powder obtained was then filtered off, washed with acetonitrile and dried. All operations were performed under an argon atmosphere, but the final material appears to be stable in air.

Complete intercalation and ion exchange were ascertained by elemental analyses, X-ray powder diffraction and IR spectroscopy. The X-ray powder diffraction pattern shows that the material obtained is highly crystalline as it exhibits sharp *hkl* reflections which can be readily indexed in a monoclinic unit cell (Table 1) closely related to that of pristine FePS₃. Parameters *a* and *b* along the plane of the layers remain essentially unchanged. The interlamellar distance increases by *ca.* 5.65 Å as a result of intercalation, which strongly suggests that the TTF species stand 'edge on' with respect to the FePS₃ slabs, with the C=C binary axis parallel to the layers, as in the FeOCl intercalates.⁸

Elemental analyses of the intercalate (noted 1 hereafter) were performed (in wt. %: Fe, 18.5; P, 12.5; S, 56.9; C, 11.1; H, 0.75). These data lead to a formula Fe_{0.82}PS₃(TTF)_{0.38} very close to Fe_{1-x}PS₃(TTF)_{2x} ($x \approx 0.18$). The TTF content is consistent with an expected value 0.39 calculated on the basis of close-packed TTF species¹² perpendicular to the layers. Infrared spectra of 1 (KBr pellets) showed evidence for the presence of TTF species (sharp bands at 1480, 830, 740 cm⁻¹, broad strong band *ca.* 1300 cm⁻¹). The ν(PS₃)

Table 1 Indexing of Fe_{0.82}PS₃(TTF)_{0.38}, at room temperature. Cell dimensions, *a* = 5.919 Å, *b* = 10.348 Å, *c* = 12.642 Å, β = 107.45°

spacing/Å		<i>hkl</i>	intensity
obs.	calc.		
12.02	12.06	001	m
6.030	6.030	002	w
3.015	3.015	004	w
2.943	2.943	130	s
2.762	2.762	131	s
2.496	2.496	132	m
1.725	1.725	060	m
1.706	1.707	061	m
1.657	1.658	062	w
1.488	1.489	26 $\bar{1}$	m
1.459	1.456	40 $\bar{1}$	m
1.415	1.412	400	m

asymmetric stretching band, which occurs at 570 cm⁻¹ in pure FePS₃, is split into three components at 650, 580 and 602 cm⁻¹. This band is usually split into only two components in the MPS₃ intercalates, the splitting reflecting the presence of intralamellar metal vacancies.²

The d.c. electrical conductivity, σ, of 1 along the plane of the layers was measured in the range 110–370 K, using classical four-probe techniques. Large quasi-monocrystalline (giving sharp X-ray reflections) platelets of the intercalate were prepared following the procedure described above, but increased the reaction duration by a factor of *ca.* 3. Gold electrodes were deposited on the platelets by evaporation under vacuum. Results are plotted in Fig. 1. The conductivity of 1 is quite large ($\sigma \approx 3 \Omega^{-1} \text{ cm}^{-1}$ at 25 °C) and does not

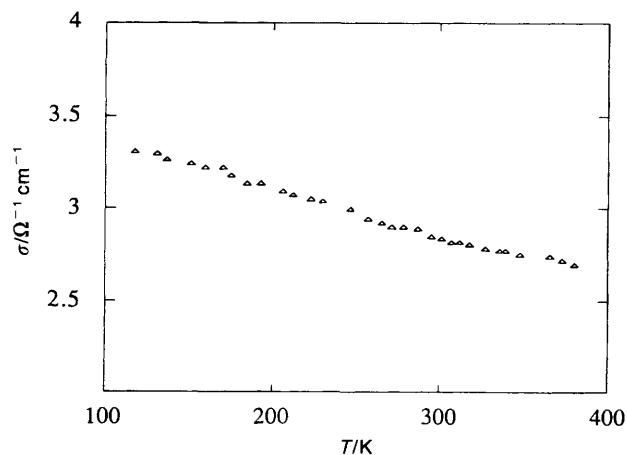


Fig. 1 Temperature dependence of the d.c. electrical conductivity of 1

appear to be thermally activated. Indeed, σ increases as the temperature is lowered, a behaviour which indicates a metallic character for 1.

Such a metallic character sharply contrasts with the semiconducting properties of pure FePS_3 (and more generally of all MPS_3 materials).¹³ It also contrasts with the semiconducting properties of the previously studied MPS_3 -TTF intercalates where $\text{M}=\text{Mn}, \text{Cd}$.¹ The different behaviour of the present intercalate might therefore be related to the ability of the intralayer Fe^{II} cations to be partially oxidized by the interlayer TTF^+ species. Such charge transfer would result in mixed valency on both the host and the guest sublattices. This view is supported by preliminary results of a ^{56}Fe Mössbauer study which provides evidence for the presence in 1 of some Fe^{III} cations.¹⁴

References

- 1 R. Clement, *J. Chem. Soc., Chem. Commun.*, 1980, 647.
- 2 R. Clement, O. Garnier and J. Jegoudez, *Inorg. Chem.*, 1986, **25**, 1404.
- 3 R. Clement, L. Lomas and J. P. Audiere, *Chem. Mater.*, 1990, **2**, 641.
- 4 P. Lacroix, J. P. Audi re and R. Clement, *J. Chem. Soc., Chem. Commun.*, 1989, 537.
- 5 M. R. Antonio and B. A. Averill, *J. Chem. Soc., Chem. Commun.*, 1981, 382.
- 6 H. Van Damme, F. Obrecht and M. Letellier, *Nouv. J. Chem.*, 1984, **8**, 681.
- 7 S. M. Kauzlarich, B. K. Teo and B. A. Averill, *Inorg. Chem.*, 1986, **25**, 1209.
- 8 S. M. Kauzlarich, J. L. Stanton, J. Faber Jr. and B. A. Averill, *J. Am. Chem. Soc.*, 1986, **108**, 7946.
- 9 J. F. Bringley, J. M. Fabre and B. A. Averill, *J. Am. Chem. Soc.*, 1990, **112**, 4577.
- 10 W. Klingen, R. Ott and H. Hahn, *Z. Anorg. Allg. Chem.*, 1973, **396**, 271.
- 11 F. Wudl, *J. Am. Chem. Soc.*, 1975, **97**, 1962.
- 12 W. F. Cooper, N. C. Kenny, J. W. Edmonds, A. Napel, F. Wudl and P. Coppens, *J. Chem. Soc., Chem. Commun.*, 1971, 889.
- 13 R. Brec, *Solid State Ionics*, 1986, **22**, 3, and references therein.
- 14 R. Clement, W. R. Dunham and A. H. Francis, to be published.

Communication 1/00866H; Received 22nd February, 1991