Dibenzenechromium as a Reagent for Ready Insertion of Large Amounts of Chromium into Solid Layered $FePS_3$

René Clement,*[a] Odile Garnier,[a] Hélène Mercier,[a] Jean-Paul Audiere,[a] Alain Michalowicz,[b] Bernard Rousseau,[c] and Ralph Setton[c]

[a] *Laboratoire de Physicochimie Minérale and ERA 672, Université Paris-Sud, 91405 Orsay, France*
[b] *Laboratoire de Physicochimie Structurale, Université Paris Val de Marne, 94000 Creteil and Lure, Orsay, France*
[c] *Centre de Recherches sur les Solides à Organisation Cristalline Imparfaite CRSOCI, CNRS, 45045 Orleans Cedex, France*

Treatment of lamellar $FePS_3$ with $Cr(\eta^6\text{-}C_6H_6)_2$ yields a series of semiconducting $FePS_3Cr_xC_y$ materials ($0.5 \lesssim x \lesssim 2$, $x \simeq y$) which contain Cr^{III} ions bound to the sulphur atoms.

Transition metal phosphorus trisulphides MPS_3, where M is a divalent metal cation, form a class of lamellar semiconductors,[1] with each layer made up of ethane-like $P_2S_6^{4-}$ units co-ordinated to M^{2+} cations. These materials exhibit a versatile intercalation chemistry and two types of intercalation compounds have been described, both of them containing cationic guest species: (i) those where the negative charge of the layers arises from a loss of M^{2+} intralamellar cations;[2] (ii) those where the negative charge of the layers arises from a guest → host electron transfer.[3,4] We show in this communication that intercalation of dibenzenechromium [$Cr(\eta^6\text{-}C_6H_6)_2$ or $Crbz_2$: an electron donor species] into $FePS_3$ is the first step of a mild process which leads eventually, *via* decomposition within the interlamellar space of the organometallic guest, to solid materials, $FeSP_3Cr_xC_y$, of an unusual type.

Intercalation of $Crbz_2$ into several MPS_3 compounds has already been reported by one of us.[5] However, the reaction was carried out at a temperature (*ca.* 130 °C) such that no noticeable decomposition of the guest molecule occurred, and an intercalation compound $FePS_3|Crbz_2|_{0.32}$ was formed. We now report that if the same preparation (reaction of $FePS_3$ with a deoxygenated toluene solution of $Crbz_2$ in a sealed ampoule) is carried out at a slightly higher temperature (*ca.* 150 °C), all the $Crbz_2$ dissolved in the solution is taken up by the $FePS_3$ sample, provided the $Crbz_2 : FePS_3$ ratio is kept below *ca.* 2. Black, air stable solids are obtained, which may be described by the formulation $FePS_3Cr_xC_y$ ($x \simeq y$), according to elemental analysis.† *X*-Ray powder diffraction shows that the interlamellar distance, which reaches about 12.38 Å in $FePS_3(Crbz_2)_{0.32}$, has now collapsed to about 6.42 Å, irrespective of the chromium and carbon content. This value is the same value as for pure $FePS_3$. This fact clearly demonstrates that there are no longer any dibenzenechromium entities between the layers, a conclusion confirmed by the i.r. spectra of the samples, which no longer show any of the

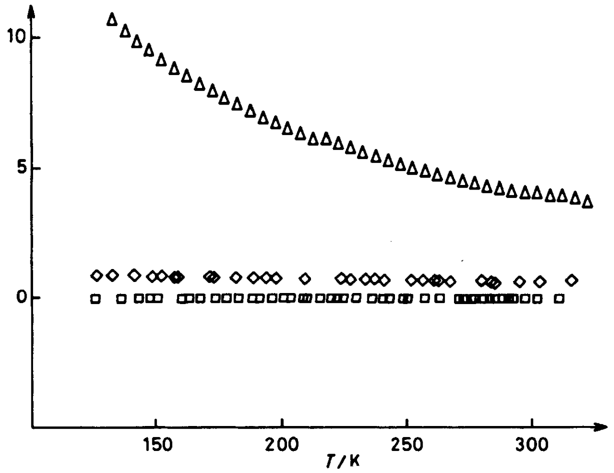

Figure 1. Temperature dependence of the resistivity ρ (expressed in Ω. cm) of (△) pure $FePS_3$ and of (◊) $FePS_3Cr_{1.1}C_{1.1}$ and (□) $FePS_3Cr_{1.7}C_{1.7}$.

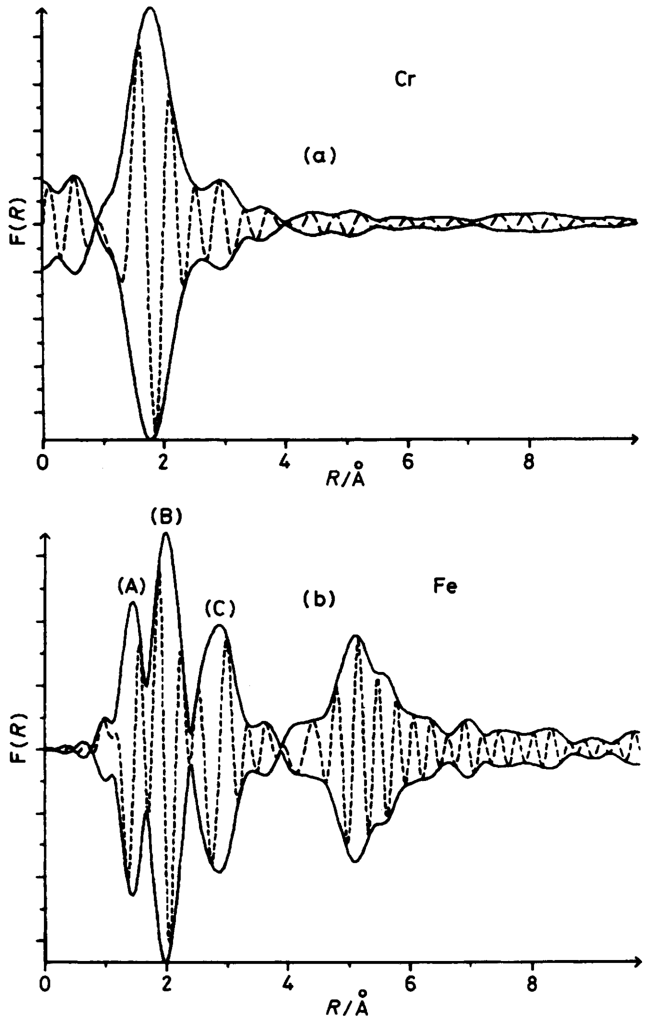

Figure 2. (a) Radial distribution function F(*R*) around chromium obtained by a Fourier transform of EXAFS experimental data on (**1**). (b) Radial distribution function F(*R*) around iron in (**1**). The large wide peak at *ca.* 5—6 Å is interpreted as the result of multiple scattering and hence does not correspond to actual bonds. For classical reasons,[7] the *R* scale on both graphs does not correspond to actual lengths and hence only bond distances mentioned in the text must be considered.

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† Satisfactory analyses have been obtained for several stoicheiometries from $x = ca.\ 0.5$ to $ca.\ 1.8$. The Cr and C contents were systematically very close to each other. Analyses also gave a small hydrogen content of *ca.* 0.5%, which is not taken into account in the formulation, because it is so small.

bands of $Crbz_2^+$, but still show a sharp strong band at 570 cm^{-1} characteristic of the asymmetric $\nu(PS_3)$ stretching.[6]

Conductivity measurements were performed between 120 and 325 K on quasi monocrystalline platelets of the samples. The results (Figure 1) show that the semiconducting properties of $FePS_3$ are modified greatly, by insertion of Cr/C. Indeed, the resistivity of the derivatives is much lower than that of pure $FePS_3$, is almost temperature independent ($\rho_{100\ K} = ca.\ 2\ \rho_{300\ K}$), and does not depend strongly on the composition.

$FePS_3Cr_{1.1}C_{1.1}$
(1)

Complete structural determination is precluded by the large number of defects introduced by the reaction process. An extended *X*-ray absorption fine structure (EXAFS) study at both iron and chromium edges was therefore undertaken on a sample having the intermediate composition $FePS_3Cr_{1.1}C_{1.1}$, **(1)**. The radial distribution functions F(*R*) around chromium and iron are shown in Figures 2(a) and 2(b) respectively. The peak in Figure 2(a) reflects the bonding between the chromium atoms and the sulphur atoms of the layers. Using a fitting procedure already described,[7] the data can be accounted for by assuming a Cr–S distance equal to 2.37 ± 0.02 Å, a value which strongly suggests that chromium is in the +III oxidation state.[8] Additional information confirms this conclusion. (i) The energy position of the *X*-ray absorption edge of a given atom is known to be very sensitive to the oxidation state of this atom.[9] We compared the energy at the *K* absorption edge of chromium in **(1)** and in the layer compound $CrPS_4$, known to possess Cr^{III} ions located at the centres of slightly distorted S_6 octahedra.[10] Both edges were found at the same energy and even exhibit the same pre-edge fine structure. (ii) A comparative *X*-ray photoelectron spectroscopic (XPS) study of **(1)** and of $CrPS_4$ was performed (VG ESCALAB Mark 5 spectrometer), and the $2p_{3/2}$ binding energy of chromium was found at 575.2 ± 0.2 eV in both compounds.

In contrast to chromium, the radial distribution function F(*R*) around iron in **(1)** exhibits several peaks (A), (B), and (C), Figure 2(b). Comparison with $MnPS_3$[11] suggests that peak (B) represents the Fe–S bonds, while (C) represents unresolved Fe–P and Fe–Fe distances. Standard fitting procedures yield 2.55 Å for the Fe–S distances, *i.e.* exactly the same value as in pure $FePS_3$.[12] More puzzling is the observation of peak (A) which reveals the occurrence of a short distance in the co-ordination sphere of at least a fraction of the iron atoms. Taking into account the chemical analysis, this new EXAFS peak can only be explained by assuming the existence of Fe–C bonds, 2.12 Å in length.

Although a complete description of these new materials cannot yet be given, it nevertheless seems clear that collapse of the layers and ready decomposition of intercalated $Crbz_2$ are driven by the co-ordination of the resulting Cr^{III} ions to the sulphur atoms in the layers. The fundamental question arising is how the layer structure accommodates the large number of electrons released upon the $Cr^0 \rightarrow Cr^{+III}$ process. The general problem of guest → host electron transfer in the MPS_3 has not yet been satisfactorily solved. We point out that the occurrence of Fe–C bonds might be a consequence of the formation of carbide ions during the decomposition of $Crbz_2$. Such species would act as counterions for the Cr^{III} species and lower the extent of guest → host electron transfer.

Preliminary experiments have shown that other layered chalcogenide systems undergo similar reactions. This work could thus open a new field at the interface of solid state and organometallic chemistry and may lead to new materials with unusual properties.

Received, 10th July 1984; Com. 996

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