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Preparation and characterization of diamine intercalation compounds of misfit layer sulfides

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Polycrystalline $(PbS)_{1.18}(TiS_2)_2$, a composite misfit layer sulfide, reacts directly with ethylenediamine (en) and propylenediamine (pn) to form intercalation complexes of compositions $(PbS)_{1.18}(TiS_2)_2(en)_{0.44}$ and $(PbS)_{1.18}(TiS_2)_2(pn)_{0.37}$, respectively. Attempts at preparing pure intercalate phases with *n*-alkyldiamines of longer chains failed. These novel intercalation compounds were examined by various techniques including XRD, FTIR, XPS, TG and TPD measurements. The XRD results are consistent with an intercalation model where the organic molecules are present at every TiS_2–TiS_2 interface, as monolayers with the alkyl chain almost parallel to the sulfur layers. Deintercalation of the diamines occurs at about 250 °C and releases H_2S simultaneously. The formation of H_2S has been associated to a direct attack on the lattice by water molecules since the complexes, as revealed by IR and XPS, readily absorb water under ambient conditions. Moreover, N 1s spectra of intercalated samples, prepared either bringing the host into contact with the liquid diamine or by dosing with diamine vapors in the spectrometer′s preparation chamber, revealed the presence of two types of organic molecules differently bound to the chalcogenide. This behavior departs from that observed in the *in situ* deposition of diamine vapors onto an oxidized aluminium surface. In this case, the N 1s spectrum exhibits a single peak of lower binding energy indicative that the amine molecule is weakly bound to the surface.

Introduction

Misfit layer sulfides of formula $(MS)_{1+\delta}(TS_2)_2$ (M = Ln, Pb, Sn, Bi; T = Ti, Nb, Ta) are a new class of composite layered compounds whose structures consist of two successive TS_2 sandwiches alternating with an MS double layer –MS–TS_2–TS_2–MS–TS_2–TS_2– stacked along the *c*-axis. Owing to the slightly different dimensions of sublattices MS and TS_2, these phases exhibit incommensurate structures. An excellent review that includes a detailed structural and physical description based, among others, on electrical and magnetic properties (*e.g.* superconductivity) was recently published by Wiegers.[1] In addition to these relevant properties, this family of compounds features van der Waals gaps at the interface between two adjacent TS_2 slabs. Within these gaps, octahedral and tetrahedral interstitial positions are created that can be occupied by different guest species. This property has attracted our group's attention in the last few years; investigations have shown that these composite systems can act as intercalation lattices towards both atomic and molecular guest species.[2–5]

Among these misfit layer sulfides, the $(PbS)_{1.18}(TiS_2)_2$ compound, whose structure has been fully characterized from X-ray single crystal studies,[6] possesses an unusually high structural flexibility despite the presence of PbS layers intercalated between two consecutive TiS_2 slabs. Although this increases layer thickness in this compound, which changes from three planes of strongly bonded atoms in the binary sulfide, TiS_2 –(S–Ti–S)–, to seven planes –(S–Ti–S–Pb–S–Ti–S–)– in $(PbS)_{1.18}(TiS_2)_2$ [thus increasing rigidity against transverse layer distortion[7]], the region bound by the TiS_2–TiS_2 interface in this ternary sulfide can accommodate guest molecules such cobaltocene,[4] *n*-alkylamines ($C_nH_{2n+1}NH_2$ with *n* up to 9);[5] also the sodiated phases[8] can cointercalate propylene carbonate thus causing a lattice expansion that exceeds by 12.4 Å the dimensions of the repeating unit PbS–TiS_2–TiS_2.

The aim of this work has been contribute new data for the interaction of nitrogenous bases molecules with these layer sulfides. Based on the above described behavior, we chose $(PbS)_{1.18}(TiS_2)$ as our prototype. This paper reports the preparation of novel intercalates with linear aliphatic diamines and their characterization by using various analytical techniques. Results concerning the electronic modifications in the host introduced by the guest molecules, and their influence on transport properties, will be published in a subsequent paper.

Experimental

Polycrystalline samples of $(PbS)_{1.18}(TiS_2)_2$ were prepared by heating mixtures of the corresponding elements (supplied by Strem Chem.) in appropiate amounts in evacuated silica tubes. Further details concerning heating steps and temperatures are given elsewhere.[4,6] The compound, obtained as small plate-like crystals with a metal luster, was manually ground in an agate mortar. All amines were of reagent grade (supplied by Aldrich); they were further purified by distillation under argon and stored with molecular sieve 0.3 nm (supplied by Merck). About 100 mg of the starting sulfide were sealed with 1.5 ml of *n*-alkyldiamine in a Pyrex tube and heated at 60 or 90 °C for pn (1,3-diaminopropane) and en (1,2-diaminoethane) intercalates, respectively, for 24 h. The absence of (00*l*) reflections from $(PbS)_{1.18}(TiS_2)_2$ was taken as the criterion for thorough intercalation. Products were filtered and washed with pure acetonitrile. All these manipulations were carried out in a dry-glove box, where the intercalates were dried and stored. Elemental analyses were conducted on a Fisons CHNS analyzer. Thermogravimetric analyses (TG) were performed on a Cahn 2000 thermobalance under a dynamic argon atmosphere. Temperature programmed deintercalation (TPD) measurements were carried out on a quartz reactor coupled to a quadropole mass spectrometer (on sensorlab model VG). The gas carrier used was argon. IR spectra were recorded on a Bomem MB-100 FTIR system using KBr pellets containing about 1% of product. Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D-5000 Instrument using graphite monochromated Cu-Kα radiation and operating at 40 kV and 30 mA. For identification purposes, intensities were collected at 0.02 (2θ) intervals using 0.06 s per step. For broadening analyses of reflection lines, intensities were recorded in the same scan step at a time of 3.6 s per step.

XPS spectra were recorded on an ESCALAB 210 spectrometer operating in the constant pass energy mode (50 eV) and using unmonochromatized Mg-Kα (1253.6 eV) radiation as excitation sources. The pressure in the analysis chamber was always below 10^{-9} mbar. Samples, made into pellets by compressing the powdered compounds at about 3 tonnes under an argon atmosphere, were stuck onto a copper holder with the aid of a low vapor pressure epoxy resin (Torr.Seal from Varian) and transferred to the spectrometer's preparation chamber ($P \approx 10^{-7}$ mbar). Prior to analysis, samples were scraped with a corundum file for several minutes to remove surface contamination and to expose clean, fresh surfaces. Because of the epoxy resin layer, all samples exhibited charging effects of 2–3 eV. The binding energy (E_b) reference was taken at 161.7 eV for the S 2p core level, since this element was present in all the compounds studied. These binding energy values were consistent with those previously reported for S^{2-} species.[9]

Results and discussion

The synthesis of $(PbS)_{1.18}(TiS_2)_2$ provided a pure material consistent with the reported X-ray diffraction pattern.[4,6] On treatment with the *n*-alkyldiamines, particles swelled (see Fig. 1) and preserved their black colour but lost their metallic luster. The XRD patterns for the en and pn intercalates showed the disappearance of the starting material and the formation of new compounds whose particles were strongly oriented along the *c*-axis. Thus, the XRD patterns (Fig. 2) only contained peaks associated with (00*l*) reflections, thus preventing a comprehensive evaluation of the unit-cell constants for these intercalates. The periodic length values calculated from these reflections, *d*, which define the thickness of the PbS–TiS_2–TiS_2 unit stacked along the *c*-axis, are shown in Table 1. We failed to synthesize pure intercalates of diamines of longer chain length. In fact, two diamines *viz.* butyldiamine (bn) and heptyldiamine, tested as guest compounds led to partial intercalation [see Fig. 2(d)], even when the synthesis temperature was raised to 200 °C in the case of heptyldiamine.

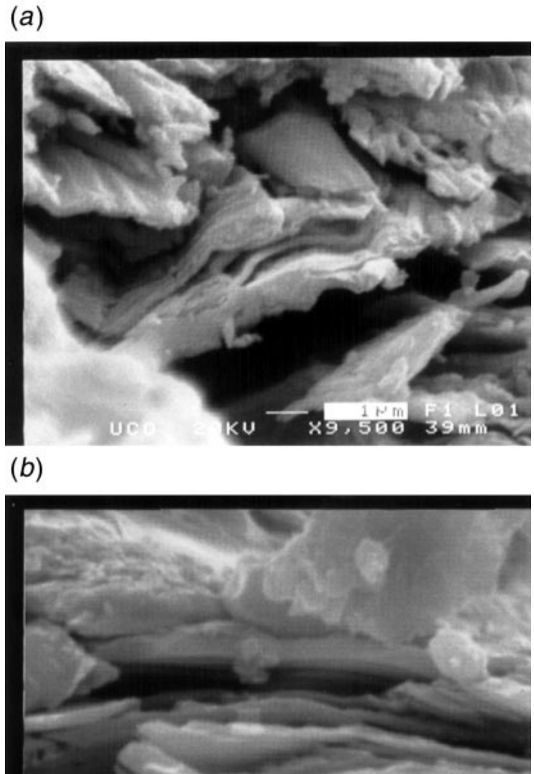

Fig. 1 SEM image of (a) en complex and (b) pn complex. The crystals are predominantly oriented with their layers parallel to the view direction.

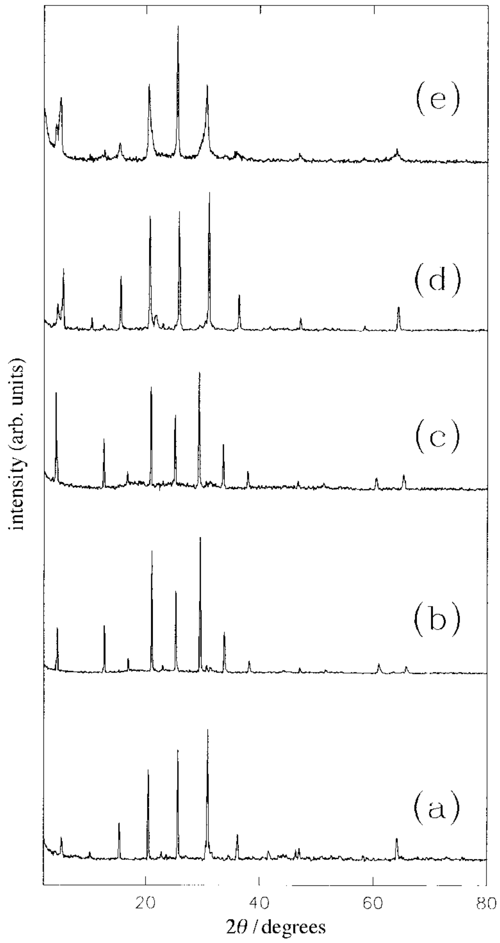

Fig. 2 XRD patterns for (a) $(PbS)_{1.18}(TiS_2)_2$, (b) $(PbS)_{1.18}(TiS_2)_2$-$(en)_{0.44}$, (c) $(PbS)_{1.18}(TiS_2)_2(pn)_{0.37}$, (d) $(PbS)_{1.18}(TiS_2)_2(bn)_x$ and (e) $(PbS)_{1.18}(TiS_2)_2(en)_{0.44}$ heated at 400 °C.

It is worth noting the small difference in interlayer expansion (*e.g.* Δd changed from 3.62 Å in en to 4.32 Å in heptyldiamine) exhibited by the four intercalates despite the increased chain length. These values are quite similar to those obtained in the intercalation of *n*-alkylamines[5] and reveal the little influence of the hydrocarbon chain length. Moreover, the increase in interlayer spacing is slightly larger than the van der Waals diameter of the amine group (*ca.* 3.4 Å). These results suggest that the $-(CH_2)_n-$ axis in the diamine molecule is nearly parallel to the sulfur layers. In fact, excellent correlation between the interlayer distance and the number of carbon atoms in the alkyl chain (n_c) was observed for en, pn and bn intercalates. The straight line obtained fits the equation [$\Delta d = 3.16 + 0.23 n_c$ ($r = 1.000$)]. Since the alkyl chain length increment in the all-*trans* conformation is estimated to be 1.27 Å per additional carbon atom, it is reasonable to assume that the

Table 1 Analytical and structural data for pristine $(PbS)_{1.18}(TiS_2)_2$ and diamine complexes

	Analysis[a] (%)					
Compound	C	N	H	S	Periodic length/Å	P.D.
$(PbS)_{1.18}(TiS_2)_2$	—	—	—	33.0(32.8)	17.45	—
$(PbS)_{1.18}(TiS_2)_2(en)_{0.44}$	2.04(1.98)	2.30(2.31)	0.71(0.66)	30.8(29.8)	21.11	0.894
$(PbS)_{1.18}(TiS_2)_2(pn)_{0.37}$	2.52(2.49)	1.87(1.94)	0.71(0.69)	32.6(32.3)	21.37	0.890

[a] Calculated values are given in parenthesis.

diamines are present as monomolecular layers with their longitudinal axis tilted by an angle of arcsin (0.23/1.27) = 10° relative to the sulfur layers.[10]

In addition to changes in the positions of the diffraction peaks observed upon intercalation, the originally rather sharp lines for the pristine compound broaden, thus indicating the formation of smaller crystallites and/or an increase in elastic strains in the host lattice. In order to quantify the microstructural changes induced by the intercalation process, $(00l)$ profiles were analysed by the integral breadth method[11] for separation of size and strain broadening. The analysis was based on eqn. (1)

$$(\delta 2\theta)^2 \cos^2\theta = 16\langle e^2\rangle \sin^2\theta + (k^2\lambda^2/L^2) \qquad (1)$$

where $\delta 2\theta$ is the integral breadth after correction of the instrumental broadening obtained for a highly crystalline silicon powder, $<e^2>$ denotes local strains (defined as $\Delta d/d$, d being the interplanar spacing), L is crystallite size and k is a near-unity constant related to crystallite shape. The slope $16<e^2>$ and intercept $k^2\lambda^2/L^2$ were used to determine the distortion and size parameters.

Fig. 3 shows plots for different reflections of original and intercalated samples. The crystallite sizes and strains calculated from these plots are given in Table 2. These data warrant several comments. First, the plot for the pristine layer sulfide had a negligible intercept and slope, thus indicating that the size of coherently diffraction domains, L, was large and the microstrains content, $<e^2>$, low, both of which are consistent with a highly crystalline powder. After the amine intercalates, the microstrain content increases significantly (about 50 times) as reflected by an increase in the slope. Second, the intercept values hardly change, thus suggesting that the amine intercalation does not alter significantly the size of the coherent diffraction domains. This means that the main contribution to line broadening is that of local strains probably due to the expansions required to accommodate the amine in the interlayer spacing.

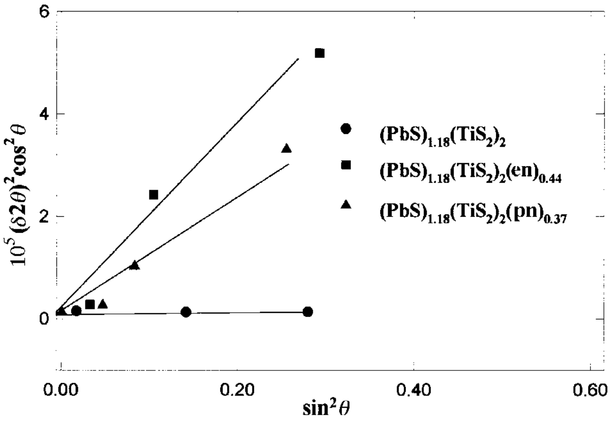

Fig. 3 Plot of $(\delta 2\theta)^2\cos^2\theta$ *vs.* $\sin^2\theta$ of (●) $(PbS)_{1.18}(TiS_2)_2$, (■) $(PbS)_{1.18}(TiS_2)_2(en)_{0.44}$ and (▲) $(PbS)_{1.18}(TiS_2)_2(pn)_{0.37}$.

Table 2 Crystallite size and microstrain contents for pristine $(PbS)_{1.18}(TiS_2)_2$ and diamine complexes

Compound	L/Å	10^6 $<e^2>$
$(PbS)_{1.18}(TiS_2)_2$	2500	0.004
$(PbS)_{1.18}(TiS_2)_2(en)_{0.44}$	2388	11.6
$(PbS)_{1.18}(TiS_2)_2(pn)_{0.37}$	2077	7.8
En complex (400 °C)	359	12.2
Pn complex (400 °C)	457	36.0

The amine contents in the intercalates, obtained by C,H,N analyses, are shown in Table 1. It is worth noting the acceptable agreement between experimental and calculated figures. Interestingly, these intercalates have amine contents higher than those in *n*-alkylamine complexes of the same hydrocarbon length. This differential stoichiometry is consistent with the much stronger basic properties of dialkylamines and their better coordination ability relative to *n*-alkylamines. Available information on the reactivity of TiS_2 towards *n*-alkyldiamines for comparison with the intercalation properties of the ternary sulfide is scarce. In fact, the sole reference found was published very recently.[12] For this reason, we undertook a study of the intercalation with en by direct reaction of TiS_2 under the same experimental conditions used in the preparation of misfit layer intercalates. Surprisingly, only partial conversion was achieved after the same reaction time. In fact, the product was a mixture of a new c-axis expanded phase and the pristine compound. The c-axis separation, $\Delta d = 4.08$ Å, is slightly greater than that in the $(en)_x(PbS)_{1.18}(TiS_2)_2$ intercalate and smaller than the calculated interlayer separation (16 Å) for an all-*trans* chain orientation. Partial intercalation was also obtained with heptyldiamine; however, the interlayer expansion observed, 6.14 Å, was much greater than that in the $(PbS)_{1.18}(TiS_2)_2$ intercalate. Our results contrast with those recently reported by Ogata *et al.*[12] in two main points. First, these authors obtained complete reaction by heating at 120 °C for 20 h. Second, they found a clear loss of sulfur. The composition determined was $TiS_{1.761}(en)_{0.296}$ and $TiS_{1.385}(en)_{0.271}$ for powder and crystal samples, respectively. Our complexes prepared hardly changed in sulfur content of the pristine $(PbS)_{1.18}(TiS_2)_2$ as the differences between experimental and calculated percentages were within the experimental error of the analytical method (see Table 1). In any case, the dramatic decrease in sulfur content found by Ogata *et al.*[12] questions the preservation of the host structure.

We have no clear explanation for the smaller tendency of TiS_2 to intercalate en directly. Particle size as a factor for this differential behavior can be discarded since the average particle size of TiS_2, as revealed by SEM, is at least one order of magnitude smaller than that of the ternary sulfide. Alternatively, the smaller tendency of TiS_2 to undergo a direct reaction with the organic compound should be a result of the difficulty in preparing highly stoichiometric TiS_2. In our case, the real composition of the sample used, as determined from TG measurements, was $Ti_{1.028}S_2$. This means that some interstitial positions located at the van der Waals gap are occupied by the additional titanium atoms, which affect the same positions available for amine intercalation. In any case, this behavior is nothing special since intercalation of *n*-alkylamines into TiS_2 is only feasible if the disulfide is pretreated with hydrazine.[13]

In contrast to TiS_2, TaS_2 either in 2H or 6R polytype, intercalates en fairly well.[14,15] The reported stoichiometry for both systems is $TaS_2[en]_{1/4}$. If we adopt this system as reference, the amine content per transition metal atom measured in $(PbS)_{1.18}(TiS_2)_2$ is smaller than that found in binary chalcogenides. These differences in amine stoichiometry were also found with ethylamine as the guest species and were ascribed to the electron donation of MS layers to the TS_2 sublattice, which reduces the electron accepting ability of TS_2 and thus decreases the amine uptaking capacity of the host.

The packing density of the amine intercalates (P.D.) was determined by combining the amine content with the cross sectional area of the amine molecule[16] and the area of the basal plane of TiS_2 sublattice unit cell.[6] The results thus obtained are shown in Table 1. Both intercalates have a similar packing density that is less than unity. This reveals the existence of a significant fraction of empty sites in the interlayer space. These sites should be accessible to other molecules and dictate the ease with which water is absorbed by these intercalates as shown below.

The stability of the intercalates was studied from TG data obtained under a dynamic argon atmosphere and the analysis of evolved gases by mass spectrometry. Fig. 4 shows TG and TPD curves recorded over the temperature range 25–400 °C. The total weight loss from en and pn intercalates was 5.0 and 6.4% respectively, and hence somewhat greater than that corresponding to the amine release (especially from the propylenediamine complex). The main weight loss occurred over a wide temperature range, *viz.* 150–400 °C, and corresponds to the appearance of the amine base peak. The peak profiles are fairly broad and asymmetric as the likely result of differences in bonding interactions between the organic molecules and the sulfur layers. In fact, the en complex is somewhat more stable than the pn complex (peak temperature 280 and 245 °C, respectively) and the deintercalation temperatures clearly exceed those of the *n*-alkylamine complexes.[5] This means that diamines are more strongly bonded within the layers owing to the presence of two donor groups in the molecule. Indeed, above 400 °C the product still exhibits very weak reflections of the intercalate [Fig. 2(e)] and the residual amine content is further confirmed by elemental analysis. One other interesting finding is the appearance of H_2S simultaneously with diamine release. This is a common feature in thermal amine deintercalation[17] and, among the different models that account for H_2S release,[18] spectroscopic data support a direct attack on the lattice by water molecules according to the following reaction:

$$H_2O + S^{2-}{}_{(\mathrm{lattice})} \rightarrow H_2S + O^{2-}{}_{(\mathrm{lattice})} \qquad (2)$$

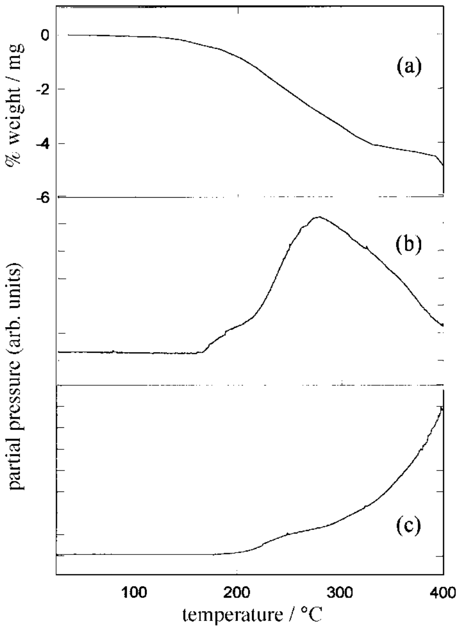

Fig. 4 Thermal deintercalation data for the en complex. (a) Thermogravimetric curve, (b) temperature programmed deintercalation spectra for amine (*m*/*z* 30) and (c) H_2S (*m*/*z* 34) base peaks.

The origin of this water, which could not be detected by MS owing to the water background, can be inferred from the suggestion of Joy and Vasudevan[19] concerning the feasibility of an exchange reaction between physically adsorbed water picked up during the transfer of the intercalated material to the TG or TPD apparatus, and the intercalated amine molecules. In our samples, the wate uptake is favoured by the empty sites in the interlayer space owing to the low packing density. In this context, IR spectra provide valuable information on this hydration reaction in spite of the poor resolution of the absorption peaks resulting from the high absorbances of the samples. Fig. 5 shows the Fourier transform IR spectra. A broad, strong band centered at 3450 cm^{-1} is consistent with OH stretching and a weak, broad band at *ca.* 1630 cm^{-1} associated to H_2O bending. The strong band has a shoulder centered at *ca.* 3220 cm^{-1} that can be ascribed to NH stretching (free diamines exhibit two sharp peaks at 3350 and 3209 cm^{-1}[20] corresponding to asymmetric and symmetric N—H stretching, respectively). The shifts towards lower frequency might be indicative of bonding interactions of the amine molecules within the layers, probably with the Ti *via* the nitrogen lone pair. The presence of the amine is further confirmed by the appearance of bands at 2960, 2855 and 1442 cm^{-1} that correspond to stretching and bending of the CH_2 groups. On heating the pellet at 100 °C *in vacuo*, the IR spectrum in air maintained basically the same features except for a significantly increased intensity in the broad band at *ca.* 3250 cm^{-1}, ascribed to the amine groups. Simultaneously, the band close to 3500 cm^{-1} decreased in intensity. These spectroscopic data are consistent with the ease of water uptake by the amine intercalates and, together with the simultaneous release of amine and H_2S, suggests strong association between amine and water molecules.

Further evidence of the interaction of water with the host lattice was obtained from XPS data. Table 3 lists the binding energies of the emission peaks for the host and intercalates. Minimal changes were observed in the S 2p and Pb 4f profiles. In fact, the binding energy and full width at half maximum (fwhm) of the Pb 4f peak were found to remain constant upon the amine intercalation, whereas the width of S 2p broad peak increased slightly during the process (see Table 3). By contrast, the Ti 2p spectra underwent significant changes (see Fig. 6).

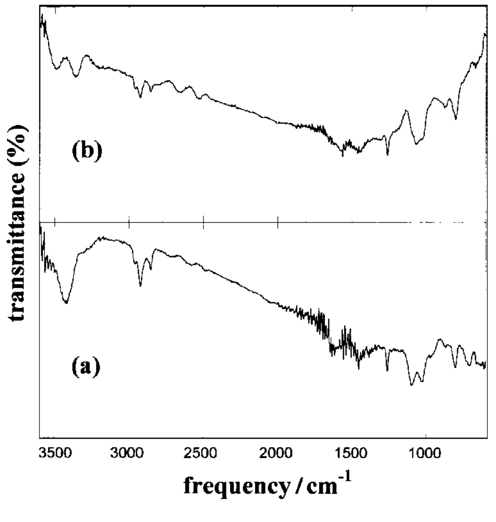

Fig. 5 FTIR spectra recorded in air for (a) $(PbS)_{1.18}(TiS_2)_2(en)_{0.44}$ as prepared and (b) heated at 100 °C for 24 h.

Table 3 Binding energies and fwhm in eV for the main core level spectra of diamine complexes; values for the pristine compound have been included for comparison

Compound	Binding level S 2p	Pb $4f_{7/2}$	Ti $2p_{3/2}$	N 1s	C 1s	O 1s
$(PbS)_{1.18}(TiS_2)_2$	161.7(2.49)	138.1(1.62)	456.9(2.3)	—	—	—
$(PbS)_{1.18}(TiS_2)_2(en)_{0.44}$	161.7(2.55)	137.9(1.62)	457.0 459.0	402.3(2.07) 400.3(2.50)	285.8(2.80)	531.7(2.9)
$(PbS)_{1.18}(TiS_2)_2$[a]	161.7(2.55)	137.9(1.60)	456.9	402.3(2.02) 400.3(2.40)	285.8(2.95)	—
Al_2O_3–Al[a]	—	—	—	399.3(2.57)	285.8(2.80)	531.5(3.1)
$(PbS)_{1.18}(TiS_2)_2(pn)_{0.37}$	161.7(2.55)	138.1(1.63)	457.1 458.8	402.2(2.14) 400.5(2.37)	286.5(3.12)	532.2(3.6)

[a] *In situ* en deposition on different substrates.

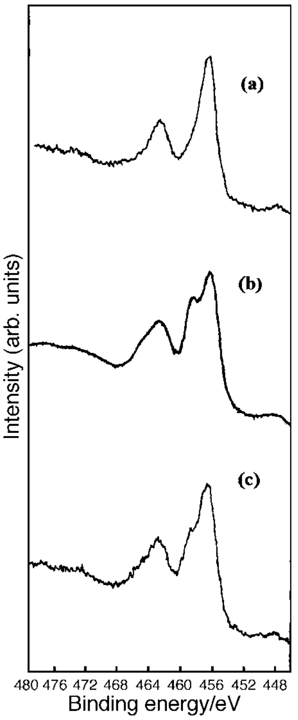

Fig. 6 Ti 2p core level spectra: (a) $(PbS)_{1.18}(TiS_2)_2$, (b) $(PbS)_{1.18}(TiS_2)_2(en)_{0.44}$ and (c) $(PbS)_{1.18}(TiS_2)_2(pn)_{0.37}$.

In addition, a pronounced Ti $2p_{3/2}$ signal coinciding with that for the pristine compound, a new component appeared at $E_b = 459.0$ eV in the intercalated phases. Based on its energy position, this component corresponds to titanium with an oxygen environment such as TiO_2[21] probably reached *via* a process such as reaction (2). Moreover, the O 1s peak in the spectrum for these samples was clearly observed as a broad signal centered at 532.0 eV that is quite consistent with reported data for OH groups and/or H_2O molecules.

Other interesting results are provided by the profiles of C 1s and N 1s spectra, the latter of which are shown in Fig. 7. In both intercalates, the broad, asymmetric C 1s core lines are accompanied by tails at the high binding energy side. This feature is more prominent for the N 1s line, which has at least two components indicative of either two oxidation states and/or two different environments for nitrogen. Application of a standard fitting procedure revealed that both components have their maxima centered at 400.4 and 402.3 eV in both amines. The lower binding energy line is slightly more intense and accounts for roughly 60% of the total intensity.

In order to acquire a better understanding of the origin of these complex profiles, two different experiments were performed in the XPS spectrometer's preparation chamber. First, en was deposited over fresh surfaces of the host at room temperature by *in situ* dosing with en vapor. Second, the test was extended to an Al surface that was actually oxidized. en was indeed adsorbed onto Al_2O_3. The N 1s spectra obtained are shown in Fig. 7, and E_b and fwhm results are collected in Table 3. Two differences are worth special comment. Thus, a broader, more asymmetric peak toward the higher E_b is observed when the substrate matrix was the sulfide. The spectrum can be also fitted to two components centered at 400.3 and 402.3 eV with an intensity ratio of 80/20. This difference in peak profiles, somewhat less pronounced, was also observed in the C 1s spectra. Furthermore, the E_b of the amine adsorbed on the Al_2O_3 surfaces is about 1 eV smaller than that of the amine deposited on the sulfide surface.

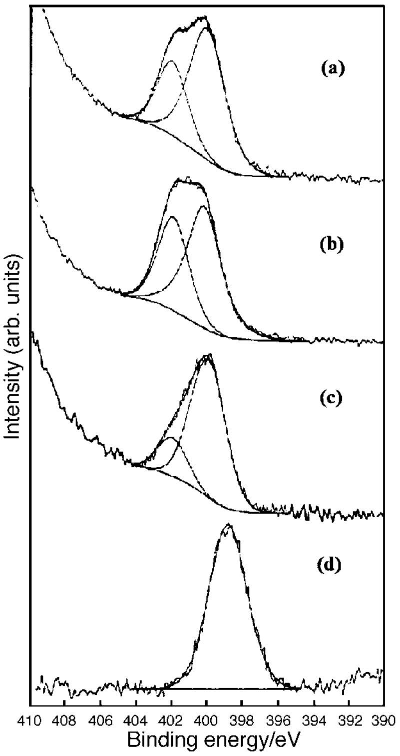

Fig. 7 N 1s core level spectra for intercalate samples in a liquid medium: (a) $(PbS)_{1.18}(TiS_2)_2(en)_{0.44}$ and (b) $(PbS)_{1.18}(TiS_2)_2(pn)_{0.37}$; and for *in situ* en deposition on (c) $(PbS)_{1.18}(TiS_2)_2$ pellet and (d) an oxidized aluminium surface.

These findings suggest differential interaction mechanisms for en molecules with the substrates. The similarity between the spectral profiles for the amine, whether intercalated in the liquid phase or deposited on the sulfide in the vapor phase, particularly in the E_b values, suggests that, notwithstanding the differential interaction procedure, the organic molecule adopts a similar coordination geometry. This is not surprising since treatment of a host material with the amine in the vapor phase is a commonplace intercalation method particularly useful with layered phosphate.[22]

The main difference lies in the relative intensity of the two components (the low energy component is more intense in the vapor deposition systems). A tentative explanation for the origin of these two components based on the E_b involves assuming that the N lone electron pair in the core levels plays a significant role. The highly symmetric N 1s and C 1s peaks found for the Al_2O_3–amine system [see Fig. 7(d)] are indicative of one type of organic molecule; also, the low E_b of the N emission suggests that the molecule is weakly bound to the surface. In fact, the value is quite similar to that reported for free diamines (398.8 eV), which increases to 400.3 eV upon coordination to a metal ion and to 401.8 eV if the nitrogen is protonated.[23,24] Although this model cannot be extended to the diamine intercalation complexes studied in this work, N 1s E_b values are quite consistent with the above described sequence.

Our results agree quite well with XPS spectra for sandwich intercalates formed from $NbSe_2$ or TaS_2 and simple nitrogenous bases.[25] In addition to broadening of the N 1s peak to an extent similar to that shown in Table 3 relative to the narrow peak (1.2 eV fwhm) for pure nitrogenous bases, Bach and Thomas[25] observed a pronounced shoulder on the high binding energy side. This was explained by assuming an electron transfer from nitrogen to the metallic layer, together with the likelihood of the organic molecule having a different configuration between the metallic layers.

Based on these observations, the following model is proposed to account for the core level spectra of the diamine–sulfide system. The first gas molecules reacting with the substrate are anchored to the host and migrate at moderated rates towards the interlayer positions defined at the TiS_2–TiS_2 interfaces, especially those located at the particle edges. We assign the peak located at higher E_b to these intercalated molecules. Strong electronic interactions between layers and the organic molecules acting as Lewis bases, through the nitrogen atom are revealed by the significantly increased E_b of the core level electrons.

Under the experimental conditions used for *in situ* dosing measurements, diffusion of the amine into the van der Waals gaps of the host must be rather slow because the lattice undergoes significant expansion to accommodate the organic molecules. This means that most deposited molecules remain strongly anchored to the host surface. The lower E_b line can be assigned to the nitrogen atom in these molecules. The core level energies suggest a stronger interaction than that obseved in the Al_2O_3 substrate. This probably reflects the outstanding ability of this sulfide to engage in intercalation reactions involving electron donor guests.

Under more severe reaction conditions (*e.g.* by bringing the solid into contact with the liquid amine) where not only the guest concentration but also the temperature is increased, one should find an increased intercalation rate. Indeed, XPS data confirm this assumption as the intensity of the higher E_b peak was significantly increased [see Fig. 7(a) and (b)].

In agreement with the presence of a least two kinds of amine differently bound to the host are the broad, asymmetric TPD profiles [see Fig. 4(b)]. This provides direct evidence of distinct guest–host interactions as revealed by the energy required for the amine release.

As mentioned above, amine extrusion by heating must severely deteriorate the host lattice as revealed by the release of H_2S and a decrease in the intensity together with a increase in the broadening of the diffraction lines. The microstructural parameters calculated from eqn. (1) support this assumption (see Table 2). Moreover, these data reveal that thermal deintercalation ruptures the diffraction domains along [001], the stacking layer direction, and significantly decreases crystallite size as a result. On the other hand, the lattice preserves its heavy distortion because, in addition to the amine release, sulfur, in a minimal amount, less than 1% of the total content, is replaced by oxygen, according to eqn. (2). In fact, the propylenediamine intercalate which uptakes water readily showed the more significant change in the $<e^2>$ parameter.

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References

1 G. A. Wiegers, *Prog. Solid State Chem.*, 1996, **1**, 24.
2 C. Barriga, P. Lavela, J. Morales, J. Pattanayak and J. L. Tirado, *Chem. Mater.*,1992, **4**, 1021.
3 L. Hernán, J. Morales, L. Sánchez and J. L. Tirado, *Chem. Mater.*, 1993, **5**, 1167.
4 L. Hernán, J. Morales, L. Sánchez, J. L. Tirado, J. P. Espinós and A. R. González Elipe, *Chem. Mater.*, 1995, **7**, 1576.
5 L. Hernán, P. Lavela, J. Morales, L. Sanchez and J. L. Tirado, *J. Mater. Chem.*, 1996, **6**, 861.
6 A. Meerschaut, C. Auriel and J. Rouxel, *J. Alloys Compd.*, 1992, **183**, 129.
7 S. A. Solin, in *Intercalation in Layered Materials*, ed. M. S. Dresseshaus, NATO ASI Series, Plenum Press, New York, 1986, p. 145.
8 P. Lavela, J. Morales and J. L. Tirado, *J. Solid State Chem.*, 1996, **124**, 238.
9 C. D. Wagner, W. M. Riggs, L. E. Davis and J. E. Muillnberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Physical Electronics Division, Eden-Prairie, 1978.
10 M. Casciola, U. Constantino, L. di Croce and F. Marmottini, *J. Inclusion Phenom.*, 1988, **6**, 291.
11 H. P. Klug, and L. E. Alexander, *X- Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, John Wiley, New York, 1974, p. 661.
12 H. Ogata, H. Fujimori, S. Miyajima, K. Kobashi, T. Chiba, R. E. Taylor and K. Endo, *J. Phys. Chem. Solids*, 1997, **58**, 701.
13 A. Weiss and R. Rothardt, *Z. Naturforsch.*, *Teil B*, 1973, **28**, 249.
14 S. F. Meyer, R. E. Howard, G. R. Stewart, J. V. Acrivos and T. H. Geballe, *J. Chem. Phys.*, 1975, **62**, 4411.
15 E. Figueroa, J. W. Brill and J. P. Selegne, *J. Phys. Chem. Solids*, 1996, **57**, 1123.
16 A. J. Jacobson, in *Intercalation Chemistry*, ed. M. S. Whittingham and A. J. Jacobson, Academic Press, New York, 1982, p. 229.
17 J. W. Johnson, *Physica B*, 1980, **99**, 141.
18 P. A. Joy and S. Vasudevan, *Chem Mater.*, 1993, **5**, 1182.
19 P. A. Joy and S. Vasudevan, *J. Am. Chem.Soc.*, 1992, **114**, 7792.
20 Y. Kargona and D. Richeson, *Chem. Mater.*, 1996, **8**, 480.
21 H. Martínez, C. Auriel, D. Gonbeau, M. Loudet and G. Pfister-Guillouzo, *Appl. Surf. Sci.*, 1996, **93**, 231.
22 A. Menéndez, M. Bárcena, E. Jaimez, J. R. García and J. Rodríguez, *Chem. Mater.*, 1993, **5**, 1078.
23 F. Parmigium and L. E. Depero, *Struct. Chem.*, 1993, **5**, 117.
24 C. Ferragina, A. La Ginestra, M. A. Massucci, G. Mattogno, P. Patrono, P. Giannoccaro, P. Catarelli and M. Arfelli, *J. Mater. Chem.*, 1995, **5**, 461.
25 B. Bach and J. M. Thomas, *J. Chem. Soc.*, *Chem. Commun.*, 1972, 302.

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