

Interaction of Aniline and Benzidine with Layered Solids $M^{n+}(\text{UO}_2\text{XO}_4)_n \cdot z \text{H}_2\text{O}$ [$M = \text{H}_3\text{O}^+, \text{Cu}^{2+}, \text{VO}^{2+}, \text{Fe}^{2+}$; $X = \text{P}, \text{As}$]

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Abstract. The layered acid solids of formula $\text{H}_3\text{UO}_2\text{XO}_4 \cdot 3 \text{H}_2\text{O}$ ($X = \text{As}, \text{P}$) intercalate aniline and benzidine arylamines, by protonation of the guest molecules. The intercalates maintain the original laminar structure.

The insertion of aniline and benzidine in the metal derivatives $M(\text{UO}_2\text{XO}_4)_2 \cdot n \text{H}_2\text{O}$ ($M = \text{Cu}, \text{VO}, \text{Fe}$) requires rather drastic conditions. Near and medium infrared spectra of intercalates in which $M = \text{VO}^{2+}$ and Cu^{2+} , indicate that the polymerization and/or oxidation of sorbed amines occurs; however, the guest-host reactions for Fe^{2+} -derivatives are of the acid-base type.

Key words. Aniline polymerization, benzidine oxidation, uranylphosphates, uranylarsenates, intercalates.

1. Introduction

2D solid materials of different chemical nature have been employed as catalysts for oxidation and/or polymerization reactions of aromatic molecules. Among these solids, smectitic minerals [1] [2] and transition metal oxides [3] deserve emphasis. In some cases, the polymerization of organic molecules may be favoured by the presence of some metallic cations in the intracrystalline space [4]. The resultant mixed materials could show electrical conductivity, and for this reason they might be useful in electronic devices and solid-state battery applications.

This paper reports studies of aniline and benzidine interactions with $\text{HUO}_2\text{PO}_4 \cdot 4 \text{H}_2\text{O}$ (HUP), $\text{HUO}_2\text{AsO}_4 \cdot 4 \text{H}_2\text{O}$ (HUAs) and their metal-derivatives (MUP and MUAs). Aniline and benzidine monomers are very appropriate precursors of polymers used for electrical or anisotropic semiconducting materials.

The host lattices HUP, HUAs, MUP and MUAs belong to the uranium mica group. Their typical structure consists of negatively charged layers of $[\text{UO}_2\text{XO}_4]_n^{n-}$ ($X = \text{P}$ or As), separated by a staggered layer of water molecules and compensating cations [5]. These solids have a very interesting intercalation chemistry [6] [7], acid behaviour and some of them are excellent protonic conductors [8].

Different experimental conditions for the guest/host interactions were chosen so as to modify the progress of the aniline and benzidine intercalation and their polymerization.

2. Experimental

$\text{H}_2\text{O}_2\text{PO}_4 \cdot 4 \text{H}_2\text{O}$ (HUP) and $\text{H}_2\text{O}_2\text{AsO}_4 \cdot 4 \text{H}_2\text{O}$ (HUAs) were prepared by precipitation from equimolar solutions of uranyl nitrate and phosphoric or arsenic acids respectively, according to Howe and Shilton [8].

Metal uranyl phosphates and arsenates (MUP, MUAs; $\text{M} = \text{VO}^{2+}$, Fe^{2+} , Cu^{2+}) were obtained by an ionic uptake process $\text{M}^{2+}/\text{C}_4\text{H}_9\text{NH}_3^+$ that brought aqueous suspensions of $\text{C}_4\text{H}_9\text{NH}_3\text{UO}_2\text{PO}_4 \cdot 4 \text{H}_2\text{O}$ (BAUP) and $\text{C}_4\text{H}_9\text{NH}_3\text{UO}_2\text{AsO}_4 \cdot 4 \text{H}_2\text{O}$ (BAUAs) intercalates into contact with aqueous metal sulphate or acetate solutions [7]. Chemical compositions and basal spacings are shown in Table I.

The aniline and benzidine were dissolved in a mixture of 50% v/v ethanol–water and the solutions were added to HUP or HUAs for the reaction to occur. For metallic derivatives (MUP or MUAs) either liquid aniline or molten benzidine were employed. All reactions were carried out in air. The guest-host reaction conditions are shown in Table II.

In all cases, the suspensions were then filtered and the solids washed with ethanol until excess amine was eliminated. The products were air-dried and stored in a controlled environment with 50% humidity.

The amounts of retained aniline and benzidine were determined by C, N, H analysis and water content were calculated from the TG-DTA curves.

The products were investigated using X-ray diffraction (Siemens D-501 diffractometer), IR spectroscopy (Perkins Elmer 883), UV–VIS–NIR (Shimadzu 3100), differential thermal analysis and thermogravimetry (Rigaku Thermoflex apparatus).

Table I. Chemical composition and basal spacing of the $\text{M}(\text{UO}_2\text{XO}_4)_2 \cdot n \text{H}_2\text{O}$ intercalates

X = P			X = As		
M	n	d002(Å)	M	n	d002(Å)
Cu^{2+}	10.2	10.42	Cu^{2+}	11.3	10.41
VO^{2+}	11.5	11.07	VO^{2+}	14.3	12.42
Fe^{2+}	8.6	10.02	Fe^{2+}	8.6	10.08

Table II. Host/guest reaction conditions.

Host	Guest	solvent	molar ratio	reaction temp.	reaction time
$\text{H}_2\text{O}_2\text{XO}_4 \cdot 4 \text{H}_2\text{O}$	Benzidine	EtOH/ H_2O	1:5	RT	24 h
[X = P, As]	Aniline	EtOH/ H_2O	1:2	RT	24 h
$\text{M}(\text{UO}_2\text{XO}_4)_2 \cdot n \text{H}_2\text{O}$	Benzidine	none	1:4	80°C	48 h
[M = Fe, VO, Cu; X = P,As]	Aniline	none	1:16	RT	72 h

3. Results and Discussion

3.1. INTERCALATION IN HUP AND HUAs

The insertion of the aromatic amines aniline and benzidine in the HUP and HUAs host networks takes place quite slowly and with difficulty in comparison with other basic molecules such as *n*-alkylamines, ammonia, pyridine etc. [6]. Thus, aniline reacts in the vapour phase with the HUP and HUAs solids, but it requires two months to obtain an intercalate with only one crystalline phase. The reaction takes place faster with a solution of aniline or benzidine in ethanol/water mixture and with a guest-host molar ratio greater than 1:2. The diffractograms of the intercalates with different amine "charge" showed a continuous evolution (Figure 1) from a mixture of phases (host + intercalate) to a single final phase (intercalate) which was achieved with molar ratios and the reaction times shown in Table II. The chemical composition of the phases with the greatest charge of amine is given in Table III, together with the 002 and 200 reflections of the intercalated compound.

It was inferred from the composition data that the amine:HUP (or HUAs) ratio approaches unity for the aniline molecule, but this cannot be achieved with the benzidine molecule because of two main factors: (i) the large size of benzidine slows its diffusion; and (ii) the presence of two basic groups per molecule could neutralize two hydrogens at the same time.

The X-ray diffractograms of the intercalates indicate that:

- (1) The intercalation does not alter the laminar structure.
- (2) There is only one crystalline phase in the HUP + aniline, or benzidine and HUAs + aniline compounds. The phase can be indexed in the tetragonal system with the parameters shown in Table III.
- (3) The HUAs + benzidine system presents a mixture of two phases: the more abundant, with a basal spacing at 18 Å, and the less abundant, at 13.9 Å. Both phases are tetragonal and the reticular parameters of the *ab* plane are of the same magnitude. The phase at 13.9 Å appears to be the preliminary step in the insertion of benzidine, although it always coexists with that at 18 Å. As the guest-host ratio and the contact time increase, the intensity of the phase at 13.9 Å decreases, while that at 18 Å increases. However, it proved impossible to achieve a single-phase intercalate, even when saturated solutions of benzidine were used with contact times of three weeks.

Table III. Chemical compositions and d_{002} and d_{200} reflections of $\text{HUO}_2\text{XO}_4 \cdot x \text{G} \cdot y \text{H}_2\text{O}$.

Guest (G)	X = P				X = As			
	<i>x</i>	<i>y</i>	$d_{002}(\text{Å})$	$d_{200}(\text{Å})$	<i>x</i>	<i>y</i>	$d_{002}(\text{Å})$	$d_{200}(\text{Å})$
Benzidine	0.8	2.4	17.8	3.47	0.7	2.9	17.9	3.56
Aniline	1.0	0.5	10.7	3.51	0.9	1.3	10.4	3.58

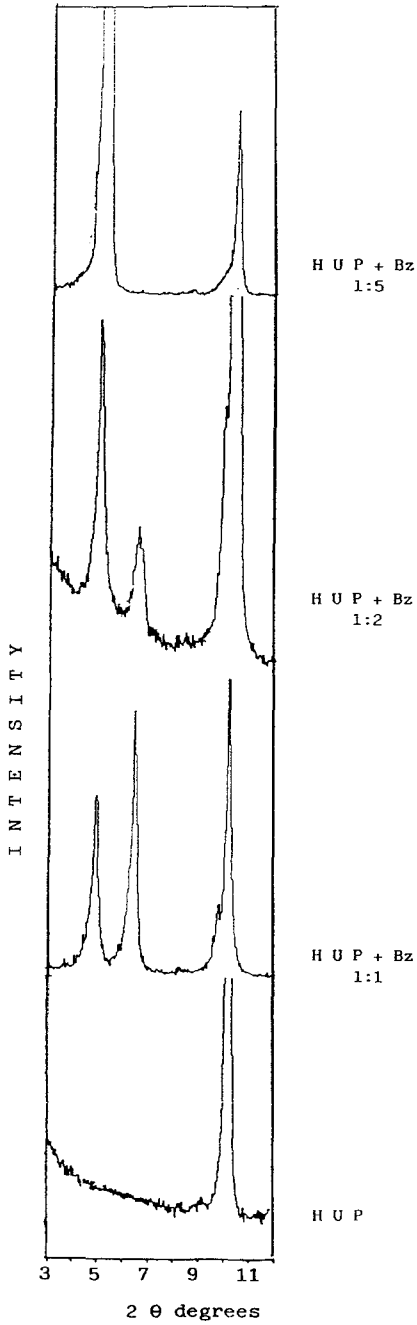


Fig. 1. X-Ray diffractograms of HUP/benzidine intercalates obtained with different initial molar ratios.

- (4) The basal spacings observed suggest that the orientation of aniline and benzidine molecules within the interlamellar space, is such that their C_2 axis (which includes the ring plane) is almost perpendicular to the layers. In the case of the HUAs + benzidine intercalate, in addition to this near perpendicular orientation, there is the possibility of the presence of another phase in which the benzidine ring plane is orientated at $\approx 50^\circ$ to the plane of the layers.

When heated at room temperature to 200°C , the intercalates eliminate water molecules without any appreciable change in the basal spacing. From this observation, it was deduced that the amine molecules form an organic pillar and that the water molecules simply occupy some of the interlayer space.

Above 200°C , this pillar is destroyed and the elimination of the guest molecule is accompanied by the 2 or 3 strong exothermic effects seen in the DTA curve (Figure 2) due to the oxidative decomposition of the organic molecules. Simultaneously, the

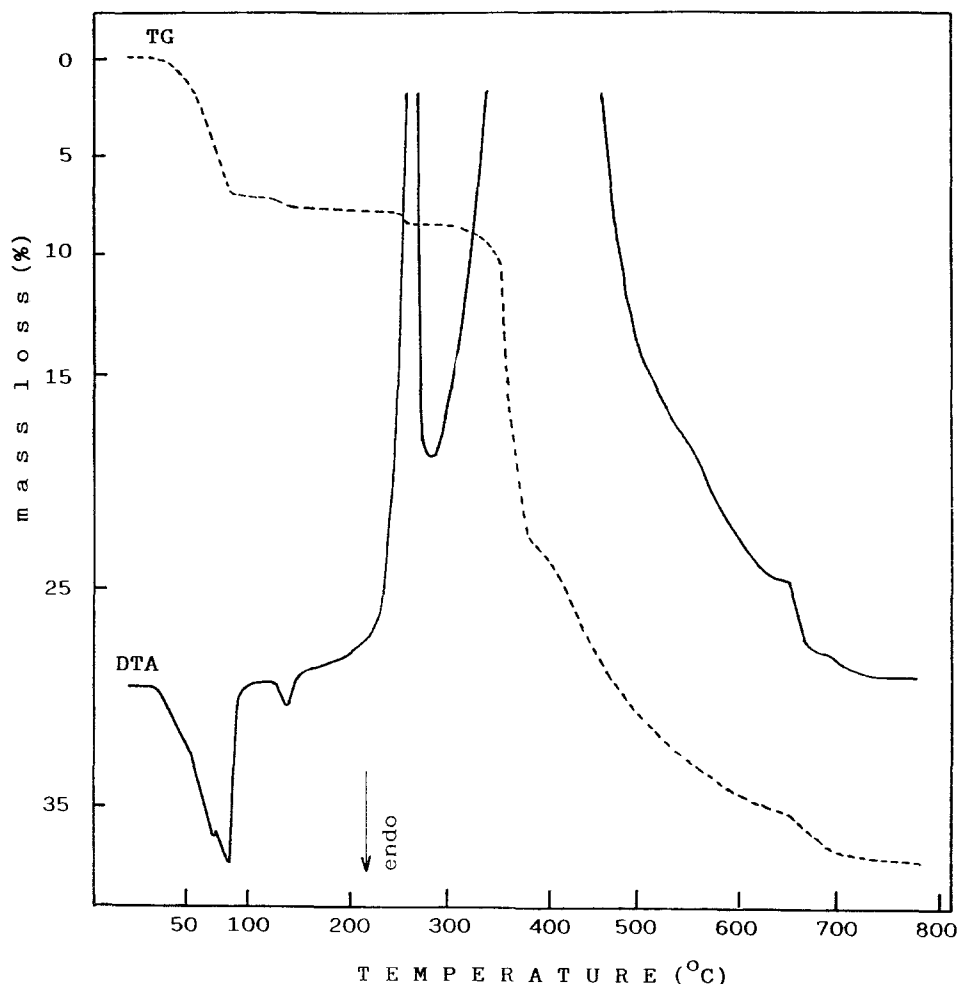


Fig. 2. DTA-TG curves of the HUP/benzidine intercalate.

TG curve indicates a continuous weight-loss up to 800°C, in HUP derivatives, and up to 500°C, in HUAs derivatives. In the latter case the loss of mass is greater than the weight of amine determined by elemental analysis suggesting that there might have been concomitant decomposition of the arsenates with the consequent elimination of As_2O_3 , as occurs with organic intercalates of other arsenates [9].

3.1.1 UV-VIS-NIR-IR spectroscopy

Spectra were recorded in the 200–50 000 nm range (50 000–200 cm^{-1}). The most significant changes takes place in the vibrational region of the spectra (NIR and IR).

The IR spectra of the intercalates HUX + NH_2Ph (X = P, or As) (Figure 3 and Table IV) show that the aniline is protonated in the interlamellar space because there are bands characteristic of the anilinium ion which correspond to the $\delta_{sym}NH_3^+$ (1500 cm^{-1}), $\delta_{asym}NH_3^+$ (1540 cm^{-1}), $\nu_{sym+asym}NH^+$ (towards 2930 cm^{-1}), and νCN (1192 cm^{-1}) modes. Moreover, out-of-plane ring deformations affected by the presence of NH_3^+ are observed: modes 4 and 11 in Wilson's notation are seen near 682 and 743 cm^{-1} , respectively, together with C—H in-plane bending (mode 3) near 1290 cm^{-1} [10]. The presence of unprotonated, free aniline is also detected, but only to a small extent since the normally intense bands due to NH_2-Ph are observed weakly near 3370 and 3240 cm^{-1} ($\nu_{sym}NH_2$), 3482 cm^{-1} ($\nu_{asym}NH_2$), 1613 cm^{-1} (δNH_2) and 761 cm^{-1} (δCH out-of-plane). In the NIR region (Figure 4) the intercalates with aniline give spectra that contain a wide band near 2150 nm which corresponds to the overlapping of the two combination bands

Table IV. Data from the infrared spectra of the intercalates.

Assignment	HUP + aniline ν (cm^{-1})	HUP + benzidine ν (cm^{-1})	HUAs + benzidine ν (cm^{-1})
$\nu_{as}NH_2$	3482 w	3425	3426
ν_sNH_2	3370, 3240 w	3336, 3230	3338, 3230
$\nu=C-H$	3068	3050	—
$\nu_{as,s}NH_3^+$	2930	2930	2903
NH_3^+	2598	2594	2593, 2361
δNH_2	1613	1629	1628
8a	1596	1602	1604
8b	1582	1580	—
$\delta_{as}NH_3^+$	1538	1557	1557
$\delta_sNH_3^+$	1506	—	1513
19a	1491	1494	1496
19b	1465	—	—
14	1326	—	1321
3	1289	1297	1297
13	1192	1273, 1217	1274, 1218
9a	—	—	1143
$\nu_{3as}PO_4^{3-}$	1121	1120	—
18b	—	—	1113
$\nu_{3s}PO_4^{3-}$	999	1000	—
18a	—	—	1007

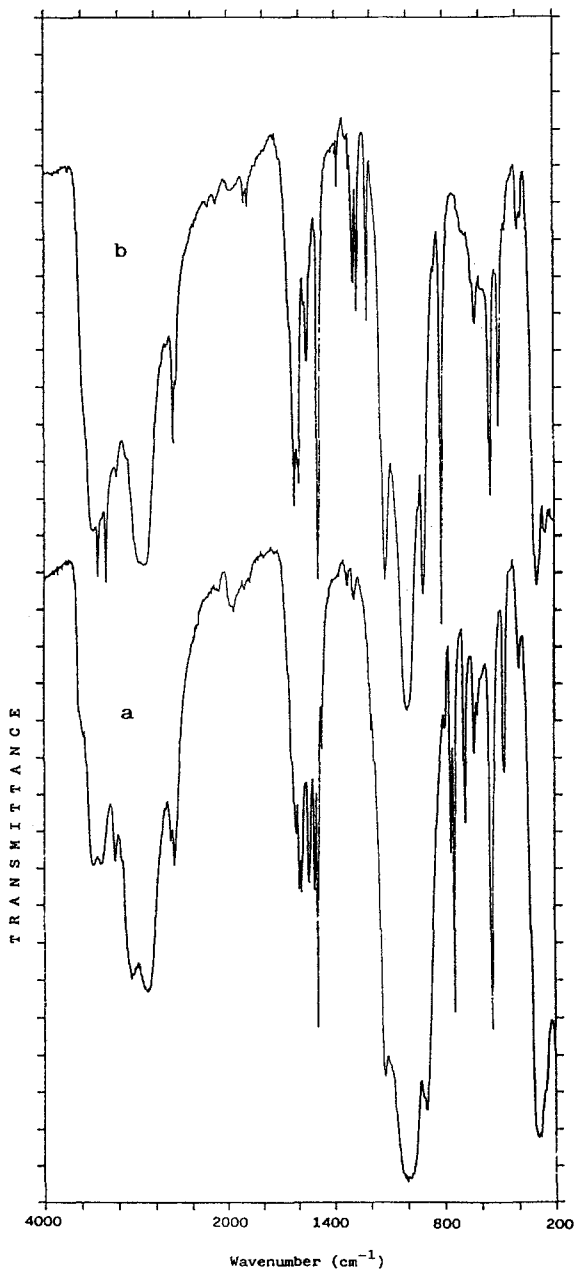


Fig. 3. I.R. spectra of: (a) HUP + aniline, and (b) HUP + benzidine.

due to NH and CH of the aniline ion. Another characteristic band of the NIR region appears near 1670 nm and is due to the first overtone of the NH⁺ symmetric stretching mode, mixed with the first overtone of CH stretching vibrations that falls within the same region. The second overtone of these bands is also observed as a very weak band near 1120 nm. In the mid-infrared region, the water bands cannot

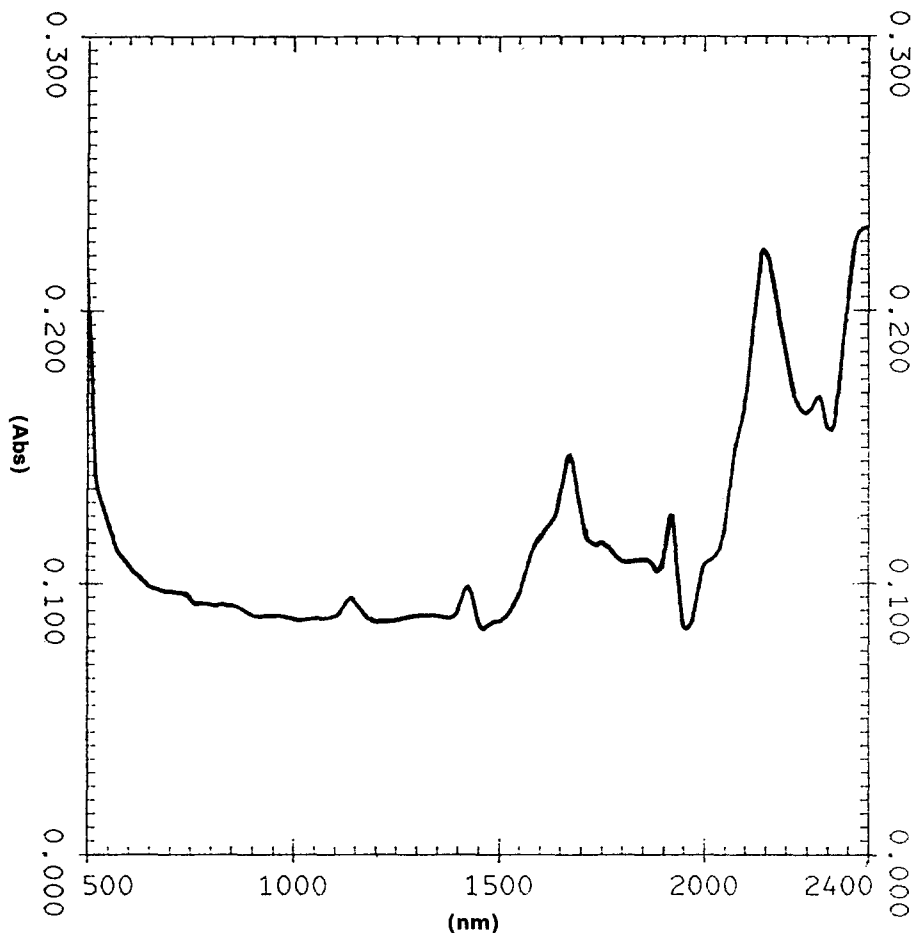


Fig. 4. Near infrared spectrum of the HUP/aniline intercalate.

be clearly seen since the 3400 and 1630 cm^{-1} zones coincide with the amine groups, but two bands are detected in the NIR region at 1915 nm and at 1420 nm ; the first corresponds to the combination of $\nu\text{ OH} + \delta\text{ OH}$, and the second to the first overtone of the OH stretching.

In contrast the results described below show that the intercalation of benzidine in the HUP and HUAs solid acids takes place through protonation of just one of the amine groups while the other remains uncharged. The HUX-benzidine intercalates (Figure 3, b) show two clear bands with similar intensities at 1273 cm^{-1} and 1217 cm^{-1} , both of which correspond to CN stretching: the first, when the amine group is free, and the second, when the amine group is associated with a proton [11]. Moreover, in the N—H vibration stretching region, two clear bands at 3400 and 3335 cm^{-1} are detected and these correspond to ν_{asym} and ν_{sym} of an NH_2 group. There is also a wide band near 2925 cm^{-1} that corresponds to the overlapping of NH^+ and $=\text{C—H}$ stretching vibration bands. Table IV displays the assignments of the observed vibrations, including the deformation

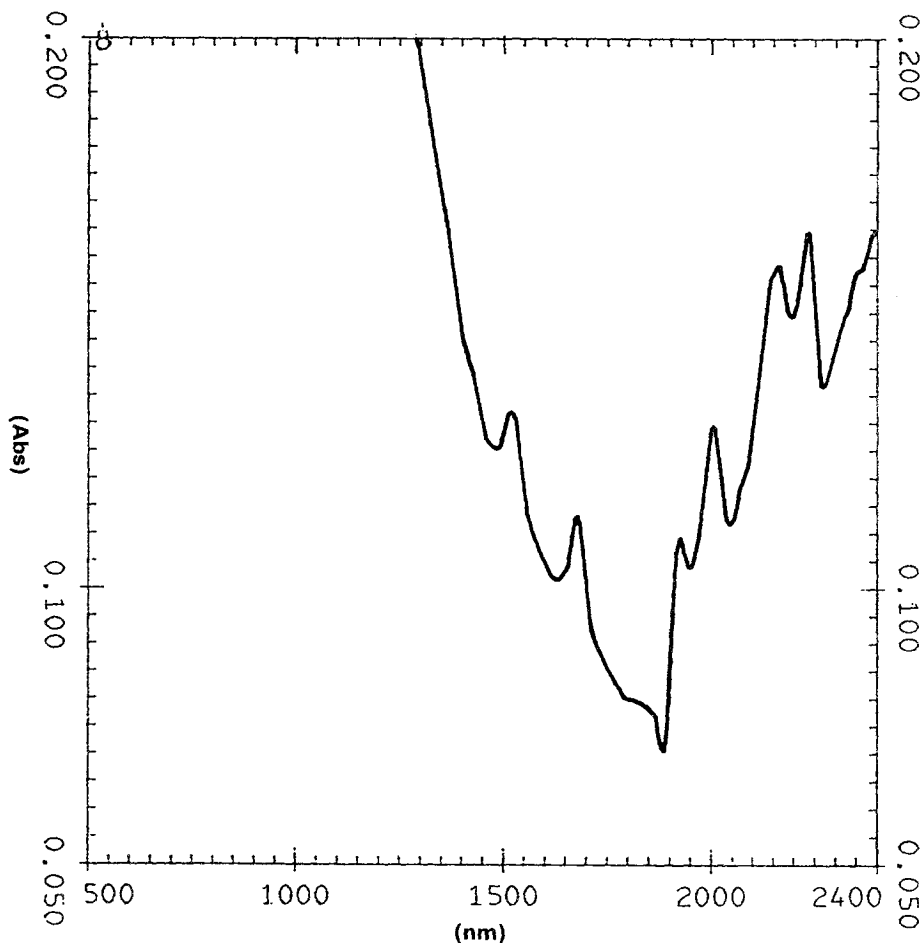


Fig. 5. Near infrared spectrum of the HUP/benzidine intercalate.

vibrations. The NIR spectrum (Figure 5) is more complicated than that of the aniline intercalates, because, together with the overtones and the combination bands of the protonated NH_3^+ group, one can see the first overtone of $\nu_{\text{sym}}\text{NH}_2$ at 1515 nm and the combined band of the δNH_2 and $\nu_{\text{asym}}\text{NH}_2$ modes at 2000 nm.

In the UV-VIS spectra of all the intercalates, in the 300–500 nm region, the vibronic bands that correspond to the uranyl ion can be seen. In the case of the benzidine intercalates, the intensity of these bands is attenuated because benzidine has absorptions in the same region.

3.2. INTERCALATION IN MUP AND MUAs

The insertion of aniline and benzidine in the metallic derivatives demands rather drastic conditions with 1:4 guest–host molar ratios for benzidine, and 1:16 for aniline. Pure organic compounds were employed: the benzidine reacted at 80°C; aniline at room temperature. The contact times in both cases were more than 48

hours. Longer contact times or higher temperatures produced final products with considerably reduced crystallinity. The composition obtained under these conditions is shown in Table V; it can be seen that the host molecules $M(\text{UO}_2\text{AsO}_4)_2 \cdot n \text{H}_2\text{O}$ retain more amine than the phosphates, but the iron derivatives of both have less tendency to absorb aniline.

Under these conditions, the reaction products are generally mixtures of two phases, one expanded, while the other, belonging to the original host, is partially dehydrated (Table VI). This suggests that intercalation is a process with a quasi-unfavourable thermodynamic equilibrium in which there is a compromise between the energy required to expand the layers and to produce molecular diffusion and the energy released in the guest–host interaction. The colour of the final products is usually black, or much darker than the starting compound. This implies a complete or partial oxidation of polymerization of the adsorbed amines that could be the key factor controlling the extent of the intercalation reaction.

The infrared spectra of the MUX + Guest (X = P, As) intercalates indicate the existence of two groups of well-differentiated intercalate compounds:

- (1) the intercalates in matrices of copper uranyl phosphate or arsenate, and those in matrices of vanadyl uranyl phosphate or arsenate (all black-colored):
- (2) the compounds derived from FeUP or FeUAs. These display very similar IR spectra to the HUP or HUAs intercalates with aniline or benzidine, that is to say, the host amine is totally or partially protonated. The protonation of the amines appears to be crucial in this intercalation process because the vibration bands of the free NH_2 group are only seen when the guest/Fe ratio exceeds unity. This result suggests that the affinity between the host and guest is associated with an acid-base mechanism and that once ArNH_3^+ has diffused into the interlamellar space, yet more amine can be intercalated, but now in the unprotonated form.

On the other hand, the CuUX and VOUX (X = P, or As) host lattices yield black intercalates which display very complex IR spectra with broad bands involving multiple vibration modes. Consequently, shifts of the vibration bands due to the 8a, 19a, 19b, 3, 13, 11, and 4 ring modes are observed. These shifts are just like those seen in aniline black and in the quinoid form of oxidized benzidine [10]; they indicate that either an oxidation or a polymerization has occurred.

Figure 6 shows the IR spectrum of the CuUP + aniline intercalate together with the wavenumbers and the assignments of some bands. According to Raupach [10], when aniline polymerizes, the vibrational modes that show most change are 8a, 19b,

Table V. Chemical composition of the $M(\text{UO}_2\text{XO}_4)_2 \cdot x \text{G} \cdot y \text{H}_2\text{O}$ intercalates.

<i>M</i>	$M(\text{UO}_2\text{PO}_4)_2 \cdot x \text{G} \cdot y \text{H}_2\text{O}$				$M(\text{UO}_2\text{AsO}_4)_2 \cdot x \text{G} \cdot y \text{H}_2\text{O}$			
	G = Aniline		G = benzidine		G = Aniline		G = benzidine	
	<i>x</i>	<i>y</i>	<i>x</i>	<i>y</i>	<i>x</i>	<i>y</i>	<i>x</i>	<i>y</i>
Cu^{2+}	2.5	3.9	0.5	9.0	2.5	8.7	0.5	7.5
VO^{2+}	1.5	8.0	1.5	6.5	4.5	5.0	1.6	6.0
Fe^{2+}	0.2	6.8	1.5	4.9	1.0	3.6	1.5	5.0

Table VI. Basal spacing and colour of intercalates.

M	M(UO ₂ PO ₄) ₂ ·x G·y H ₂ O G = Aniline		M(UO ₂ AsO ₄) ₂ ·x G·y H ₂ O G = Aniline		M(UO ₂ AsO ₄) ₂ ·x G·y H ₂ O G = Benzidine	
	d002 (Å)	colour	d002 (Å)	colour	d002 (Å)	colour
Cu ²⁺	11.0	black	17.6; 10.3	black	16.3; 10.3	black
VO ²⁺	10.2; 8.8	black	18.1; 11.0	black	10.4	black
Fe ²⁺	10.0; 8.6	green	18.1; 17.3	pale-brown	10.9; 8.7	green-brown

The bold values correspond to the most abundant phase.

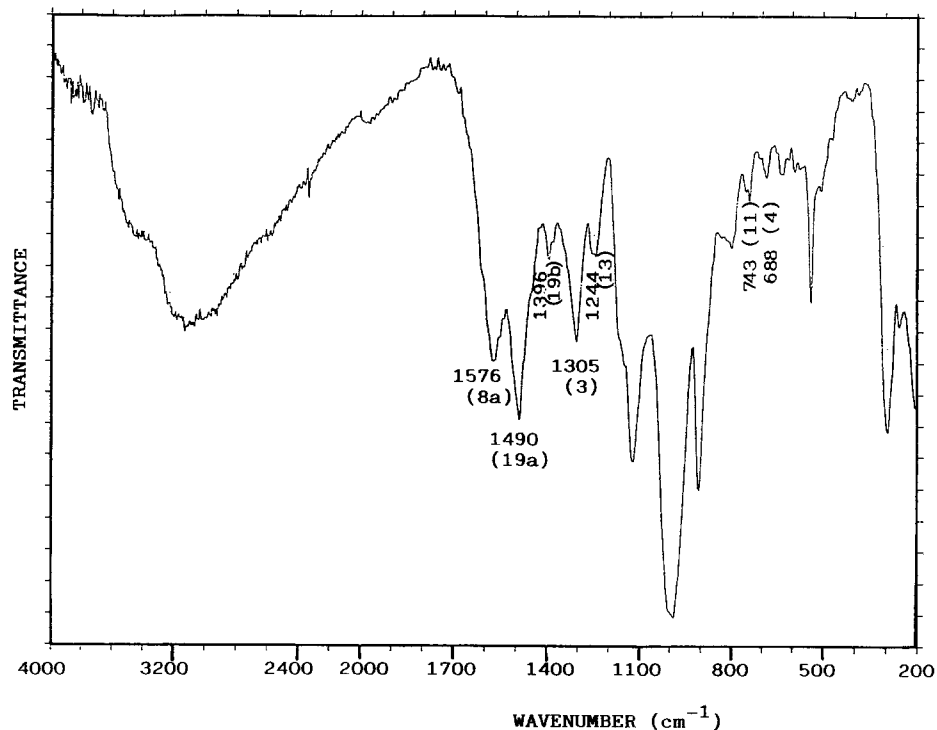


Fig. 6. I.R. spectrum of the CuUP/Aniline intercalate.

13 (C—N stretching), 9a and 11 of Wilson's notation. In the present case, the displacements are found in the same order and direction as those reported by the authors cited above. However, the existence of broad bands in the spectra of the black-colored intercalates might be an indication that, in addition to the polymerizations, other different, but less extensive, interactions such as protonation etc. may have taken place.

Because of the large number of bands in the IR spectra, these compounds present very broad poorly-defined bands in the near infra-red region (NIR).

Nevertheless, the near infrared spectra of the FeUP or Fe UAs intercalates reveal:

- the presence of free NH_2 groups, shown by the combination band of the $\delta\text{NH}_2 + \nu_{\text{as}}\text{NH}$ modes (near 1990 nm) and the first overtone of $\nu_{\text{sym}}\text{NH}_2$ near 1495 nm indicate that not all the intercalated amine is protonated; and
- the existence of a broad absorption band, near 2150 nm, that is a consequence of the overlap of the combination bands $\delta\text{NH}_3^+ + \nu_{\text{as}}\text{NH}^+$ and ring bending + CH stretching.

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