A Molecular Bronze formed by Intercalation of Benzidine in V_2O_5 Gels

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Reaction of benzidine (Bz) with V_2O_5 gel in H_2O–EtOH yields irreversibly a well-organized black intercalation compound Bz_x–V_2O_5 (plus solvation water molecules) with a maximum stocheiometry $x = 1.0$, the intercalated species being benzidine radical cations and probably oriented at a large angle with repect to the V_2O_5 planes; Bz_x–V_2O_5 and the previously reported TTF_x–V_2O_5 (TTF = tetrathiafulvalene) are the first molecular bronzes of transition metal oxides.

Several transition metal oxides such as WO_3, MoO_3, or V_2O_5, have long been known to form inclusion compounds with alkali metals.[1] These materials, termed bronzes, exhibit electronic properties (reflectivity, conductivity, *etc.*) which differ considerably from those of the parent oxides. The common elementary process responsible for this is charge transfer from the metal to the oxide lattice (although the degree of localisation of the injected charges may vary among the different species). More recently, a wide variety of hydrogen bronzes, $H_x(MO)$ (MO = WO_3, MoO_3, ReO_3, V_2O_5, TiO_2-β, *etc.*), have also been prepared *via* either solid-solution or solid–gas reaction.[2] The electronic structure of these materials is similar to that of the alkali bronzes and can also be at least partially understood in terms of charge transfer.[3]

Very recently, we showed that V_2O_5 gel reacts with tetrathiafulvalene (TTF) in an H_2O–EtOH medium to form an essentially amorphous inclusion compound.[4] The characteristic feature of TTF_x–V_2O_5 with respect to the other oxide–organic inclusion compounds reported in the literature (Lewis base–H_xMoO_3 [5] or metallicinium–V_2O_5 gel for instance [6]) is that inclusion proceeds by a charge transfer mechanism rather than by an acid–base, exchange, or solvation mechanism. In fact, it seems that TTF_x–V_2O_5 might well be the first example of an 'organic bronze'. However, TTF, its derivatives, and their seleniated analogues are very particular compounds which are able to form charge transfer salts with many inorganic anions, and the question may be raised whether or not TTF_x–V_2O_5 is a TTF salt. We therefore report here another example of charge transfer intercalation of an organic molecule (benzidine) in V_2O_5 gel, which shows that TTF_x–V_2O_5 is not a unique case and that other organic bronzes may be expected in the near future.

V_2O_5 gel was prepared by pouring the molten oxide into cold water. The Bz_x–V_2O_5 intercalate was prepared by mixing an aqueous dispersion of the gel (0.4%, w/w) with an ethanolic solution of benzidine (concentration ranging from 0 to 0.08 M). The reaction occurs within a few seconds. The black flocculated solid was centrifuged and washed with EtOH, EtOH–H_2O, and H_2O. The reaction is irreversible. Prolonged washing does not extract any additional amount of benzidine. The inclusion diagram (x *vs.* Bz/V_2O_5 ratio in the reaction mixture) is shown in Figure 1. The inclusion of TTF under the same conditions is also represented. The maximum stoicheiometry with benzidine is clearly Bz_1–V_2O_5, whereas there is no sign of saturation with TTF, even at $x = 2.9$.

In its e.s.r. spectrum, Bz_x–V_2O_5 has a very strong and narrow signal at g 2.0024, and a strong broad signal at g 1.967. The former may be assigned to the benzidine semiquinone radical cation while the latter is present in the spectrum of the pure V_2O_5 gel and may be assigned to V^{4+} ions.[7] Surprisingly, the intensity of the V^{4+} signal is not very dependent on the benzidine content.

The formation of electron-deficient species in Bz_x–V_2O_5 is confirmed by i.r. spectroscopy. The most important bands in the 2000—1100 cm^{-1} region are as follows (strong scattering of the i.r. radiation occurs in the high frequency OH, CH, and NH stretching region, and very strong bands due to the oxide lattice appear below 1100 cm^{-1}): 1650 (sh,s), 1615 (s), 1550 (vs), 1510 (sh,s), 1400 (w), 1340 (m), 1320 (m), and 1175 cm^{-1} (vs,br). They correspond neither to the spectrum of benzidine nor to that of benzidine dihydrochloride (KBr pellets). The band at 1550 cm^{-1} has been assigned to a vibration mode of the $-C-N^{+}-$ linkage, and is typical of the benzidine radical cation.[8] In fact, the spectrum of Bz_x–V_2O_5 is very similar to that of Bz–vermiculite or Bz–montmorillonite intercalates, where the radical cation is easily evidenced by its blue colour[9] (vermiculite and montmorillonite are insulating and transparent sheet silicates, whereas V_2O_5 is a deep-brown semiconducting material with an absorption edge around 600 nm). When taken together, the e.s.r. and i.r. data clearly show that inclusion of Bz in V_2O_5 gel is accompanied by an important degree of charge transfer. Surprisingly however, the d.c. conductivity of Bz_x–V_2O_5 (pressed pellets, room temperature) is not significantly different from that of V_2O_5 gel ($2.8 \times 10^{6}\ \Omega^{-1}\ cm^{-1}$).

The *X*-ray powder diffraction patterns of Bz_x–V_2O_5 exhibit a set of at least seven 00*l* reflections, corresponding to a basal spacing of 15.6 Å. No *hk* reflections were observed. The V_2O_5 gel itself has been shown by *X*-ray and electron diffraction to have a layered structure resulting from the parallel arrangement of elementary fibres into corrugated ribbons.[10] The solid V_2O_5–1.6 H_2O xerogel has a basal spacing of 11.55 Å. This corresponds most probably to a two-layer hydrate, with one layer of weakly held water molecules, and one layer of strongly held molecules, which is responsible for the 2.8 corrugation amplitude of the ribbons. A reasonable estimate for the thickness of the oxide layers is therefore 6 ± 0.2 Å. Hence, our results show (i) that inclusion of Bz is a topotactic

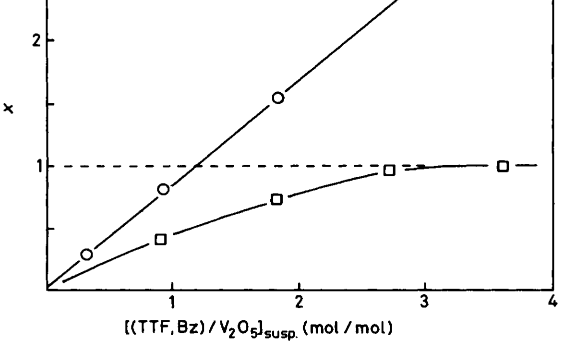

Figure 1. Inclusion diagram of benzidine (□) and TTF (○) in V_2O_5 gel; x is the organic molecule/V_2O_5 ratio (mol/mol) in the final solid.

reaction (unlike that of TTF), *i.e.* that Bz_x–V_2O_5 is a true intercalation compound, and (ii) that the interlayer space, calculated from the basal spacing and from the thickness of the layers, is *ca.* 9.6 Å (15.6 − 6.0). This is very close to the interlayer spacing in Bz–vermiculite (9.6 ± 0.1 Å),[11] where it was shown that the Bz molecules are steeply inclined to the plane of the layers. We may therefore assume that a similar molecular arrangement is achieved in Bz_x–V_2O_5.

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