Review Article:

Molecular Intercalates

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Abstract. The paper deals with the relations between host lattices and guest molecules. Several types of interaction of the guest molecules and the host material are explained and some conclusions are made about the arrangement of various guest molecules in the van der Waals' gap.

1. Introduction

Molecular intercalates are the special type of inclusion compounds which are formed by the insertion of molecules into empty sites between the layers of a layered lattice. All intercalation reactions are characterized by an expansion of the crystal lattice along the c direction perpendicular to the layers to an extent that may be correlated with the molecular dimensions of the guests and the stoichiometry of the final product. The molar ratio of guest versus host is quite often the ratio of whole numbers.

The first intercalates were prepared 150 years ago, and the first host lattice was graphite. As metals can be intercalated into graphite, their penetration between the layers is determined by the partial or total transfer of the charge to the lattice. Graphite, however, is the only host material which permits the intercalation of molecules without a lone electron pair or with a deficiency of electrons.

Other host lattices have been used from the beginning of the sixties. The most investigated lattices for these processes are the chalcogenides of the transition metals of the type MX_2, hydrogenphosphates $M^{IV}(HPO_4)_2$ or their hydrates ($M = Zr$, Sn, Ti etc.), lamellar oxide halides of transition metals of the type $M^{III}OCl$, layered oxides (MoO_3, WO_3), metal phosphorus chalcogenides $M^{II}PS_3$ ($M = Cd$, Ni, Zn, Mn), vanadyl and niobyl compounds of the type $VOXO_4$ or $NbOXO_4$ ($X = S$, P, As, Mo), layered minerals (montmorillonite, beidellite etc.) and further layered compounds.

Organic molecules containing at least one functional group are mostly used as guest molecules. This functional group mediates the anchoring of the molecules to the layers. Typical representatives of the guests are amines, alcohols, and heterocyclic compounds. Organic molecules with a very long carbon chain (C_{20}), very

voluminous molecules (1,7,10-trioxo-4,13-diaza-cyclopentadecane, voluminous complexes, and organometallic species) can also penetrate between the layers of the host lattice. The voluminous guests also include metallocenes $[M(C_5H_5)_2]$ and their derivatives formed by the substitution of the cyclopentadienyl rings. Inorganic species such as ammonia, water, some inorganic acids or their anions can penetrate between the layers of the host lattice containing oxo-anions $(Zr(HPO_4)_2, VOPO_4,$ and layered minerals). Lewis acids such as BF_3, and $HgCl_2$ can penetrate only into graphite.

It is possible to observe several types of interaction between the guest molecules and the host lattice:

(1) The anchoring of the guest can be realized by the formation of a coordination bond, the donor being the guest molecule. The coordinate bond completes a coordination polyhedron of the electrospositive atom of the layer, the resulting intercalates are named layered complexes. There are very weak Lewis bases such as amides, and isocyanides, which form very stable intercalation compounds. The stability of these systems can be explained by the ability of these guests to function as σ – donors and π – acceptors.

(2) The guest species can be anchored by the hydrogen bond which is formed between the oxygen atom of the oxo-anion of the host and the hydrogen atom of the guest species. Frequently only part of the molecules is anchored by the hydrogen bond, while another part is anchored by a coordinate bond to the most electronegative atom of the layer.
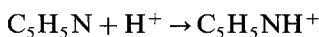
(3) The anchoring of the guest molecule can be associated with a total electron transfer to the host lattice leading to the stabilization of the product by an ionic bond between the guest cations and the negative layers. The electrons can be localized at the host lattice, which means that specific atoms of the layer are reduced [1].

$$0.16\ Co(C_5H_5)_2 + Fe^{III}OCl \rightarrow Fe^{III}_{0.84}Fe^{II}_{0.16}OCl \cdot [Co(C_5H_5)_2]_{0.16}$$
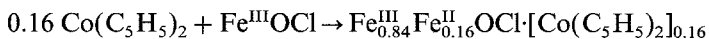
An electron can also be delocalized, which means it is transferred to the conduction band. Evidence from a variety of physical measurements has been cited in support of such a transfer. For example it was documented [2] that the intercalation of pyridine into TaS_2 leads to the oxidation of pyridine

$$2\ C_5H_5N \rightarrow C_{10}H_8N_2 + 2\ H^+ + 2e^-$$

which is associated with the formation of the pyridinium ion

$$C_5H_5N + H^+ \rightarrow C_5H_5NH^+$$

and with electron transfer.

(4) A further possibility of the anchoring of the guest molecules is by proton transfer from the host lattice to the guest molecules. This type of interaction is frequently found in layered minerals by the intercalation of hydrazine, ammonia, amines etc. The guest molecule accepts the proton from the hydroxyl group of the layer and the interaction of the cation formed with the negative layer is electrostatic.

$$Host(OH) + G \rightarrow [Host(O)]^- + [HG]^+$$

The proton transfer can also be realized by a condensation process

$$Host(OH) + H - G \rightarrow Host - G + H_2O.$$
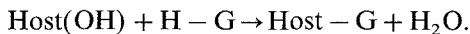
The course of many intercalation reactions is rather complicated. For example cobaltocene is oxidized to cobaltocenium by intercalation into α-Zr(HPO$_4$)$_2$, the liberated electrons reducing some of the protons from the layered lattice to elementary hydrogen [3].

$$Zr(HPO_4)_2 \cdot H_2O + 0.5\ Co(C_5H_5)_2 \rightarrow ZrH_{1.5}(PO_4)_2 \cdot [Co(C_5H_5)_2]_{0.5}$$
$$+ 0.25\ H_2 + H_2O$$
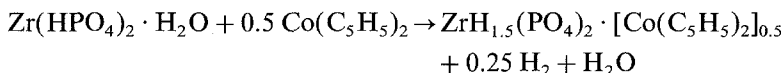
(5) Weak interactions can also be responsible for very stable intercalates. Very weak van der Waals' forces between the lattice of tellurium and iodine molecules correspond to the bond distances and interlayer distances found in the single crystal $(Te_2)_2I_2$, which is remarkably stable against water, oxygen and temperature up to 100°C [4].

2. Structural Studies

Only a few general conclusions can be drawn about the structures of the intercalates because to date only a few intercalates have been prepared as single crystals. The arrangement of the guest molecules in the van der Waals' gap is understood for most intercalates at present. From many recent papers it is possible to draw the following conclusions:

(1) The guest molecules are arranged between the layers with a minimum increase of the basal spacing if these molecules transfer completely the negative charge to the lattice or if they accept a proton from the lattice. Both these cases lead to an electrostatic interaction between the host and the guest. The minimum requirement for the increase of the basal spacing can also be connected with a translation of the layer in the xy plane [5]. Figure 1 shows that the packing of the ferrocenium cations forces a translation of the host layers by $a/2$ so that the metallocenium skeleton makes maximum use of the interlayer space. Similarly the protonated molecules of imidazole, benzimidazole or histamine [6] are placed between the negative layers so that their main symmetry plane is coplanar with the plane of the layers. The increase of the basal spacing corresponds to the 'thickness' of these molecules.

(2) A bimolecular arrangement of guest molecules with an aliphatic chain is formed if these molecules are anchored to the layer only by one coordinate bond. The increase of the basal spacing is proportional to the arrangement of the guest and their sizes, and indicates also that the oblique arrangement of the short chains changes into a perpendicular orientation of the chains with respect to the layers as the chain length increases. An even–odd alternation for the basal spacing of the tilted chains was found for all intercalates of the type VOPO$_4$·2 ROH, VOSO$_4$·2 ROH, and VOPO$_4$·2 RNH$_2$ [7, 8]. The increment in the basal spacing was bigger when going from an even to an odd carbon atom chain than from an odd to an even carbon atom chain (Figure 2). This phenomenon can be explained by the projection of the interatomic distances of the vicinal carbon atoms in the tilted chain to the axis perpendicular to the plane of the layers. Very short aliphatic chains lie parallel to the host layers. The chain lengths corresponding to tilted or perpendicular arrangements of these aliphatic chains depend on the structure of the
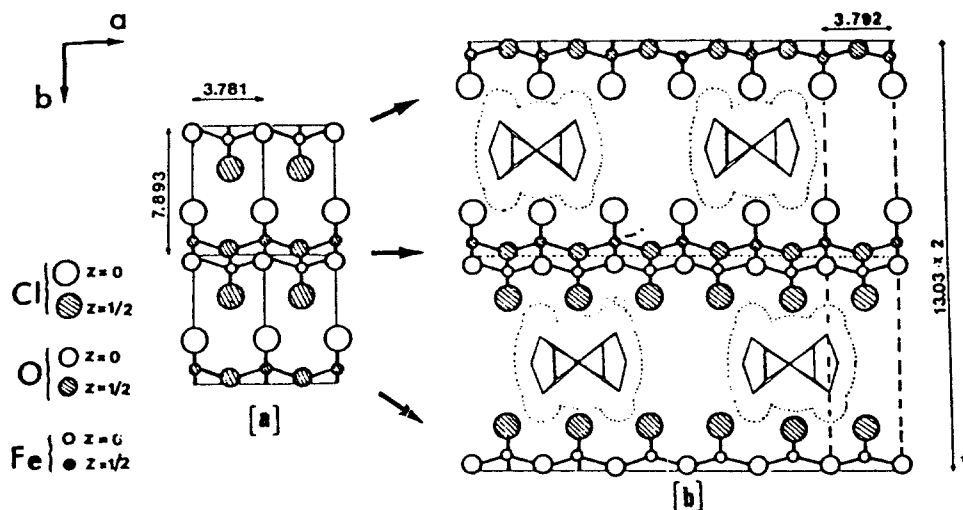
Fig. 1.   Projection on the (001) planes of the FeOCl (a) and FeOCl. (ferrocene)$_{1/6}$ (b) structures. The layers of (FeO$_4$Cl$_2$) octahedra are parallel to the (010) planes. Reproduced with permission from *Mat. Res. Bull.* [5].
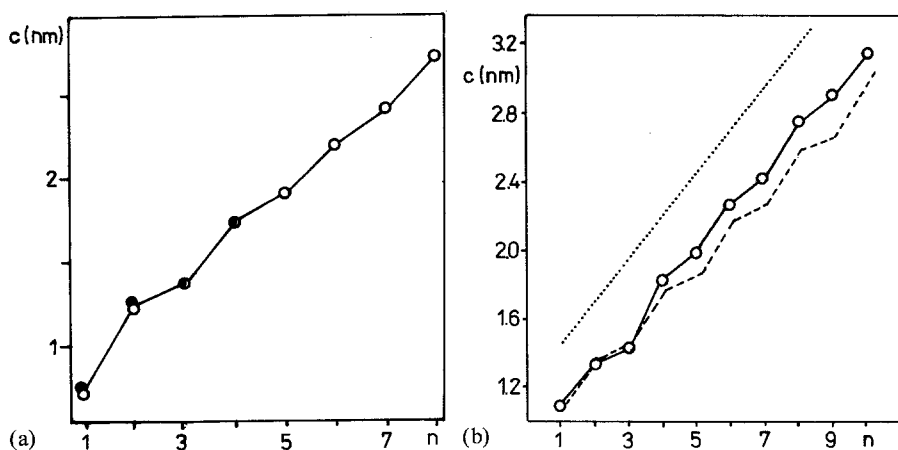

Fig. 2.   The variation of the basal spacing c with the number n of carbon atoms in the chain. (a) of VOSO$_4$·2 ROH ($\bigcirc$) and VOPO$_4$·2 ROH ($\bullet$); (b) of VOPO$_4$·2 RNH$_2$. Dotted line = bilayer perpendicular orientation of the chains. Dashed line = bilayer oblique orientation of the chains with an angle between the chain and the layers of 55°. Solid line = experimental values. Reproduced with permission from *Inorg. Chim. Acta* [7, 8].

layered host material. The compound with the longest aliphatic chain found to be lying parallel to the layers was *n*-propylamine intercalated into TaS$_2$ [9, 10] and *n*-butylamine intercalated into MoS$_2$ [11].

   The analogy between the arrangement of the aliphatic chains in the interlayer space and the arrangement of the chains on the phase interface was explained by G. Lagaly more than ten years ago [12].
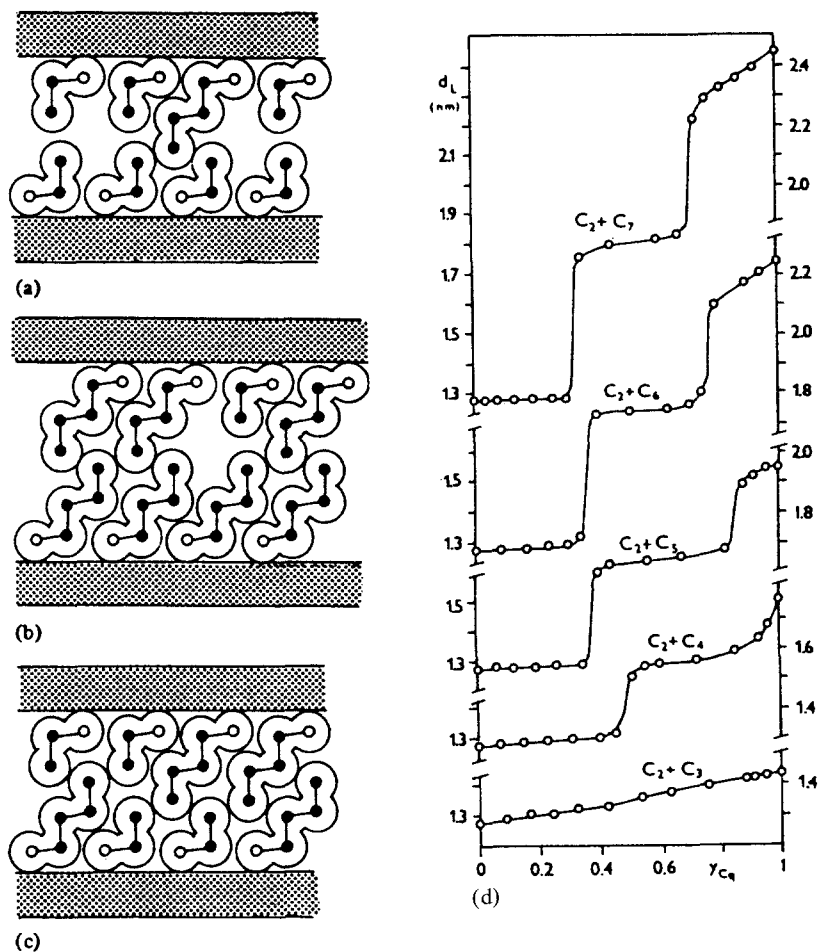
Fig. 3. Arrangement of the alcohol molecules in the mixed layered complexes $VOSO_4 \cdot (2 - x)C_p \cdot xC_q$. (a) $x \langle 000.05 \rangle$; (b) $x \langle 1.75-2 \rangle$; (c) $x \langle 0.9-1.1 \rangle$. (d) Dependence of the basal spacing d_L of the prepared solid phases on the composition of the starting liquid alcohol mixtures in the system $VOSO_4 - C_2 - C_q$ ($C_q = C_3$, C_4, C_5, C_6). Reproduced with permission from *Inorg. Chim. Acta* [14].

If the guest molecule has two functional groups in such positions that the molecule can form a bridge between the adjacent layers a monolayer arrangement is found. 1,6-Diaminohexane is anchored in this way in a seldom used host material $HTiNbO_5$ [13]. Propylamine in the same host material has the bilayer arrangement.

The intercalation of binary mixtures of aliphatic alcohols into $VOSO_4$ leads to intercalates of the formula $VOSO_4 \cdot (2 - x)C_p \cdot xC_q$, where p and q are the numbers of the carbon atoms in the aliphatic chain [14]. For $q = p + 1$ the value of x changes continuously in the interval $\langle 0-2 \rangle$, for $q \geqslant p + 2$ the ranges are $\langle 0-0.5 \rangle$, $\langle 0.9-1.1 \rangle$ and $\langle 1.75-2 \rangle$. (Fig. 3d). Figure 3a corresponds to the practically pure $VOSO_4 \cdot 2C_p$, the width of the bimolecular alcohol layer shown in Figure 3c is practically an average of the basal spacings of the intercalates $VOSO_4 \cdot 2C_p$ and

$VOSO_4 \cdot 2C_q$. The structure shown in Figure 3b corresponds to the greater variability in the content of the shorter chain alcohol compared to the long chain alcohol molecules.

The structural anisotropy of the layered materials projects the properties which depend on the structural arrangement of the lattice. The intercalation process intensifies the two-dimensional anisotropy and leads to changes of the properties which are related to the layered structure. For example the value of the ratio of the specific conductivity $\sigma_\parallel/\sigma_\perp$ is about 300 for compounds of the type MX_2, but it increases ten fold, and sometimes one hundred fold after intercalation with hydrazine or an aliphatic amine [15]. The changes of the electrical properties after intercalation of the intrinsic semicondurtors allows one to conclude that from a molecule containing one NH_2 group 0.2–0.5 electron is transferred to the lattice. The transfer of the electron from the guest to the specific atom of the host lattice is connected with changes in the electronic spectrum, while changes in the electrical properties tend to be slight.

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