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## Molecular Crystals and Liquid Crystals

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### Organic-Inorganic Molecular Composites as Possible Low-Dimensional Conductors: Photo-Polymerization of Organic Moieties Intercalated in Inorganic Layer Compounds

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ORGANIC-INORGANIC MOLECULAR COMPOSITES AS POSSIBLE LOW-DIMENSIONAL CONDUCTORS: PHOTO-POLYMERIZATION OF ORGANIC MOIETIES INTERCALATED IN INORGANIC LAYER COMPOUNDS

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We wish to draw attention to the potential for unusual electronic behaviour in composites formed on a molecular scale between organic and inorganic layer materials. Intercalation of organic molecules in inorganic layer compounds by Van der Waals or donor-acceptor interaction is common but defined stoichiometry and orientation of the organic molecules may be obtained by making salts in which organic cations are bound electrostatically to infinite inorganic anions. Many transition and non-transition metal ions M form halide (X) salts  $(RNH_3)_2MX_4$  where R is a long thin organic moiety, most simply alkyl, and the  $MX_4$  form infinite layers like a single layer of the cubic perovskite structure. A brief overview of the structures is given but we concentrate on efforts to extend the series to organic cations containing functional groups. Simplest among these are isolated double and triple bonds, e.g.  $CH_2=CHCH_2NH_3^+$  and  $CH\equiv CCH_2NH_3^+$  but diacetylenic cations have also been employed to give such salts as  $(ClCH_2C\equiv C-C\equiv CCH_2NH_3)_2CdCl_4$  and  $(C\equiv C-CH_2O_2CCH_2NH_3)_2CdCl_4$ . The latter polymerize in the solid state, the mono-amino salt much more rapidly than the di-amino.

## INTRODUCTION

There are two major reasons why low-dimensional conductors have been studied so widely and assiduously in the last few years. The first reason why they have had such an influence on physical theory, in particular, lies in the peculiar properties (especially those arising from the interaction of electrons and phonons) which are specific to one and two dimensions. The second is that the types of conducting material known to physicists have thereby been enlarged very greatly: apart from graphite itself, most of the substances whose properties form the subject of this meeting were unknown to solid state scientists ten years ago. For instance the phrase 'organic metal' contains a noun and adjective which would have sounded quite paradoxical in 1970, and with this extension in the subject matter of solid state physics has come a new emphasis on synthetic chemistry.

To these two reasons I now want to take the opportunity of adding a third, not so far examined so deeply, but which may yet prove influential in opening new domains of physical behaviour for the benefit of theory or technology. Starting from the opportunities presented by synthetic chemistry I suggest that layers or chains are uniquely suitable frameworks for building "molecular composites", namely crystalline structures that combine properties of organic and inorganic lattices on a molecular scale. An early pipe dream of this kind was Little's hypothetical model for an excitonic superconductor with its chains of conducting mixed valence inorganic material interleaved by polarisable sidechains formed of organic molecules [1]. Another might be a magnetic insulator whose properties could be changed by varying the superexchange pathway between neighbouring metal ions as a result of structural phase transitions through rotating organic sidechains. Figure 1 suggests some more possibilities.

To illustrate how molecular composites could contribute specifically to the field of low-dimensional conductors the main part of this communication is devoted to a progress report about our attempts to form oriented conjugated polymers by the solid state photo-polymerization of organic monomers. The latter are attached to the sidechains of cations held between the layers of infinite two-dimensional inorganic anions. As in most 'directed synthesis' some results are negative, though as has been wisely remarked 'no experiment is ever a complete failure: it can always serve as a bad example to others'.

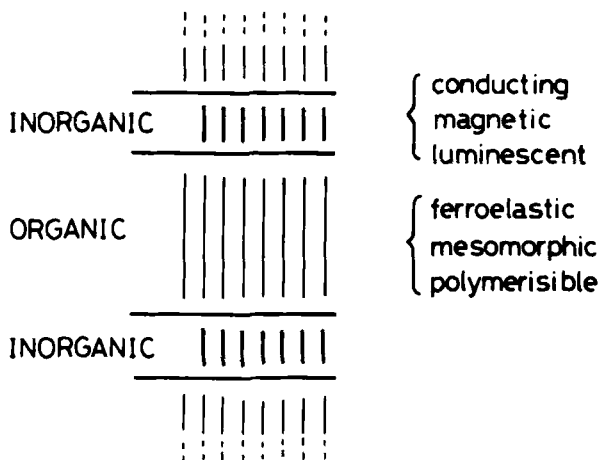
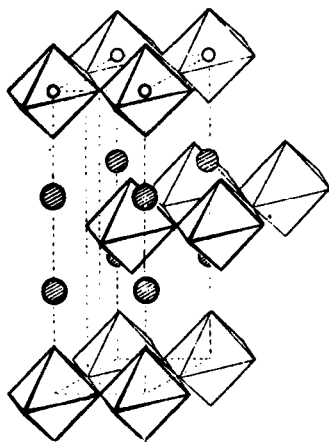
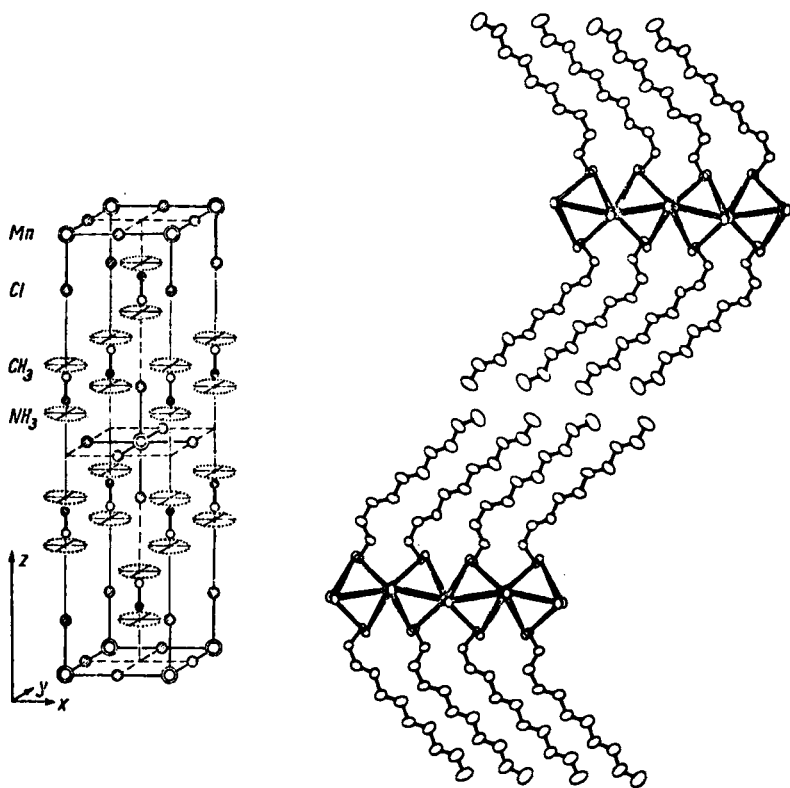


FIGURE 1 Some possible combinations of property in organic-inorganic molecular composites.

#### LAYER PEROVSKITE HALIDE SALTS

Seeking inorganic crystals containing layers which might act as templates for the photo-polymerization reactions we examined the so-called layer perovskite salts. These have the general formula  $(RNH_3)_2MX_4$  where M is a divalent metal, X a halide and R one of a wide range of organic moieties [2]. Their structures are closely related to the  $K_2NiF_4$  structure (Figure 2) which consists of square planar arrays of Ni at the centres of octahedra of F joined together through their corners. The layers are infinite anions  $(NiF_4)_n^{2n-}$  and are held together by the Group IA cations. When the latter are replaced by monoalkylammonium cations the structures of the layers remain almost unchanged, but they are forced apart. The  $-NH_3^+$  ends of the cations bind to the anion layers in specific orientations determined by hydrogen bonding with both equatorial and axial halide ions. Structural phase transitions brought about by changes in the permutations of the hydrogen bonds have been one of the central points of interest in this class of substance [3]. The other is their prototypic two-dimensional magnetic behaviour, antiferromagnetic for M = Mn, Fe and ferromagnetic for M = Cr, Cu [4]. Schematic structures of two examples (Figure 3) (R =  $CH_3$  and

FIGURE 2 The  $K_2NiF_4$  structureFIGURE 3 Structures of (a)  $(CH_3NH_3)_2MnCl_4$  [5],  
(b)  $(C_{10}H_{21}NH_3)_2CdCl_4$  [6].

$C_{10}H_{21}$ ) suggest the possibility of considerable structural flexibility in the nature of the sidechains, and also that there may be useful analogies between the long chain members of the series and the bilayers or membranes formed by polar lipids. Indeed, chain melting is observed in a number of cases [7].

In spite of the lively interest in the structures and physical properties of the layer perovskites not much effort appears to have been devoted to synthesising examples containing anything other than straight chain alkyl groups. However, as templates for stereospecific polymerizations they would seem to offer some advantages over conventional intercalates. Unlike the latter, the concentration of organic material in the solid is fixed by simple stoichiometry, as is the orientation of the molecules in the crystal.

## PREPARATIONS

### Amine Hydrochlorides

Propargylamine,  $CH\equiv CCH_2NH_2$ , and allylamine,  $CH_2=CHCH_2NH_2$ , are available commercially. Aminodiacetylenes were synthesised by us. All reactions were carried out in the dark and as close as possible to room temperature. The starting point was hexa-2,4-diyne-1,6-diol, which is photochemically stable. Two preparative routes were followed, as outlined in Table 1. In the first the diol was converted to the 1,6-dichloro-compound and thence to the 1-chloro-6-amino-compound using hexamethylenetetramine in chloroform. In the second the diol was esterified with an amino acid using dicyclohexylcarbodiimide (DCC) in ether, a reaction which has been used recently to prepare bis(carboxylic acid) esters of hexa-2,4-diyne-1,6-diol [8]. However DCC reacts with amines in the presence of carboxylic acids to produce amides [9] so we first protected the amino-group of the amino acid with  $Me_3COC(O)-(t-Boc)$  using di-tert-butyl carbonate in ethyl acetate solvent. The protecting group is readily removed under acid conditions [10].

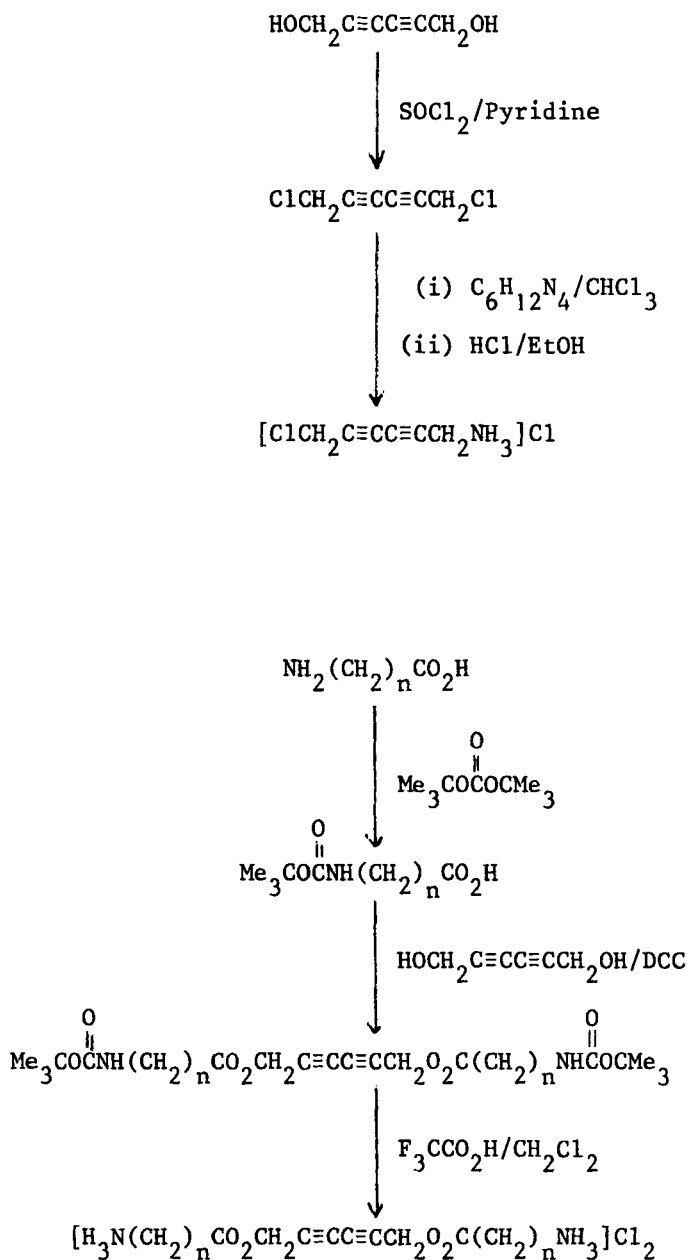
We used these two schemes to prepare a number of aminodiacetylenes but in several cases the products polymerized so rapidly that Cd salts could not be prepared. In summary, for  $RCH_2C\equiv C-C\equiv CCH_2R$  we found the following rates of polymerization in daylight at 20°C:

R

OH

very slow

Table 1. Preparative schemes for diacetylene salts





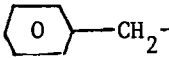
$\text{CH}_2\text{OH}$	very rapid
$\text{CO}_2\text{CH}_2\text{NH}(\text{t-Boc})$	no polymerization
$\text{CH}_2\text{CO}_2\text{CH}_2\text{NH}(\text{t-Boc})$	very rapid
$\text{CO}_2\text{CH}_2\text{NH}_2$	slow
$\text{CO}_2(\text{CH}_2)_5\text{NH}_2$	rapid

## Tetrachlorocadmate salts

Salts  $(\text{RNH}_3)_2\text{CdCl}_4$  and  $(\text{H}_3\text{NR}'\text{NH}_3)\text{CdCl}_4$  were chosen because the non-transition metal ion has no excited states in the ultraviolet in the region where the organic moieties absorb. They are prepared quite simply by mixing ethanol or aqueous ethanol solutions of the appropriate amine hydrochloride and  $\text{CdCl}_2$  [2]. In some cases (e.g.  $\text{R} = \text{CH}_2=\text{CHCH}_2-$ ) crystals grown by slow evaporation of the solvent reached 1-2  $\text{cm}^2$  area through only about 0.2 mm thickness. The crystals were clear and colourless, and showed twinning patterns under the polarising microscope very similar to those observed already in the alkylammonium salts.

Powder X-ray diffraction peaks of the new salts could all be indexed on the orthorhombic  $\text{Cmca}$  space group, as for alkylammonium salts. Unit cell parameters are listed in Table 2 with those of the ethylammonium salt for comparison. The nearly constant  $a_0$  and  $b_0$  values should be noted, together with the rapidly lengthening  $c_0$ .

Table 2. Unit-cell parameters of layer perovskite salts  $(\text{RNH}_3)_2\text{CdCl}_4$  (orthorhombic,  $\text{Cmca}$ )

R	$a_0$	$b_0$	$c_0$	$\bar{a}$
$\text{CH}_3\text{CH}_2-$	7.41	7.52	22.14	
$\text{CH}\equiv\text{CCH}_2-$	7.32	7.46	23.40	
$\text{CH}=\text{CHCH}_2-$	7.39	7.49	24.26	
	7.43	7.63	32.68	
$\text{ClCH}_2\text{C}\equiv\text{C}-\text{C}\equiv\text{CCH}_2-$	polymerized by X-rays			
$-\text{CH}_2\text{CO}_2\text{CH}_2\text{C}\equiv\text{C}-\text{C}\equiv\text{CCCH}_2\text{O}_2\text{CH}_2-$	7.37	7.46	36.30	

## PHOTOLYSIS

## Experimental Conditions

The samples, in the form either of single crystals or thin layers of compacted powder, were mounted between thin quartz plates sealed to exclude air. They were placed 1 cm from the sapphire window of a 1 kw water cooled hydrogen discharge lamp containing  $H_2$  at 10 torr pressure. The onset of polymerization was monitored by observing the samples change colour and by the appearance of new peaks in the infrared spectrum. For example, in the case of the alkyl derivative peaks due to a cyclo-butane ring would be anticipated, as in the well known solid-state dimerization of trans-cinnamic acid [11]. In the propargyl salt one would expect i.r. peaks due to double bonds if polymerization occurred to an oligo- or poly-acetylene  $\dots CH=CH-CH=CH\dots$ , while in the diacetylenic salts the well known [12] absorption of the poly-diacetylene chain would appear. Polymerization might also be brought about by X-rays.

## Results

The results of the photolysis experiments are summarized in Table 3. Briefly, no evidence was found for polymerization of the isolated double or triple bonds, either by ultraviolet or X-irradiation. On the other hand both diacetylenic salts polymerized. The 1-chloro-6-amino salt rapidly blackened in the X-ray beam so that the unit-cell parameters of the monomer salt could not be determined. Ultraviolet irradiation for 1 hour also produced a dark red product showing i.r. peaks at 1620 and  $500\text{ cm}^{-1}$  characteristic of the poly-diacetylene backbone. The tetrachlorocadmate salt of the 1,6-di(glycinate) ester polymerized only partly under the same conditions. The colour changed slightly under u.v. but became deep red under X-rays, though lines of the parent monomeric structure remained.

## DISCUSSION

No three-dimensional crystal structures are available yet for any of the new tetrachlorocadmate salts which we have made. However, it is clear from the similarity between the unit-cell parameters of the new compounds and those of similar salts whose full structures are available that our compounds have the layer perovskite structure of the type

Table 3 Photolysis results for  $(\text{RNH}_3)_2\text{CdCl}_4$ 

R	Ultraviolet [1kw $\text{H}_2$ lamp]	X-rays
$\text{H}_2\text{C}=\text{CHCH}_2^-$	None after 48 hours C=C stretch $1650\text{ cm}^{-1}$ (w) =CH <sub>2</sub> bend 1430	
$\text{HC}\equiv\text{CCH}_2^-$	None after 48 hours C $\equiv$ C stretch $2125\text{ cm}^{-1}$ (w) $\equiv\text{CH}$ 3265	
$\text{H}_2\text{gly}_2\text{-diac-}$	Pale brown after 48 hrs No change in IR C $\equiv$ C stretch $2165\text{ cm}^{-1}$ 2115	Deep red after 8 hrs Diffuse scattering increased Parent lines of orthorhombic structure remain
$\text{ClCH}_2\text{-diac-}$	Deep red after 1 hr New IR lines 500, $1620\text{ cm}^{-1}$ (polydiacetylene backbone)	Black after 8 hrs Much diffuse scattering Only 2 lines of original structure left

shown in Figure 3. Whether organic moieties attached to the sidechains lie close enough to react with one another clearly depends on the details of inter-molecular packing, which is notoriously difficult to predict. Nevertheless, some general remarks can be made.

Most important in the  $(\text{RNH}_3)_2\text{MX}_4$  series is the orientation of the N-C bond with respect to the  $\text{MX}_4$  layer, which lies between  $60$  and  $70^\circ$  in all the orthorhombic phases so far studied. If we take the structure of  $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3)_2\text{MnCl}_4$  ( $a_0$  7.29,  $b_0$  7.51,  $c_0$  25.94 Å [12]) as a guide to that of  $(\text{CH}_2=\text{CHCH}_2\text{NH}_3)_2\text{CdCl}_4$ , in view of the similarity in their unit-cell parameters, the shortest distance between doubly-bonded carbon atoms on adjacent cations could be as little as 2.7 Å in the most favourable orientation. In the propargylammonium salt, on the other hand, the closest inter-molecular approach would be much longer. Thus it is no surprise that polymerization was not observed.

In the diacetylene series there are well established criteria [12] regarding the intermolecular configurations compatible with easy polymerization. Specifically, the distance ( $d$ ) between the centres of adjacent  $C\equiv C-C\equiv C$  rods should lie between 4.5 and 5.7 Å and the angle between the rod axis and the line joining the centres of adjacent rods ( $\gamma$ ) should be in the region of  $45^\circ$ . Because it polymerized so rapidly we have no data on the unit cell dimensions of the 1-chloro-6-amino-diacetylene salt but when combined with conventional bond lengths and angles the unit cell dimensions of the 1,6-di(glycinato)diacetylene salt enable us to estimate the orientation of that cation, as shown in Figure 4. The distance  $d_0$  should equal the separation of the N atoms in the cations if they pack parallel, i.e. 5.23 Å, whilst  $\gamma$  is calculated as about  $80^\circ$ . Thus  $d$  is in the correct range for polymerization but  $\gamma$  is not. No doubt this accounts for the relative photochemical stability of the di(glycinato) salt, although there is a further constraint in that the molecules to be polymerized are held at both ends so that any configurational change is likely to break up the lattice.

## CONCLUSION

We have shown that it is possible to prepare tetrachloro-cadmium salts  $(RNH_3)_2CdCl_4$  and  $(H_3NR'NH_3)CdCl_4$  with the layer perovskite structure in which the groups R and R' contain functional groups potentially capable of intermolecular photochemical reaction, and possible polymerization. Whether the photochemical reaction occurs or not depends on fine details of molecular packing which can only be examined by preparing a much wider range of compounds. Further extensions of the structural principle of organic-inorganic molecular composites would be to use transition metal ions having their own magnetic or luminescent behaviour. Such studies are in progress in our laboratory.

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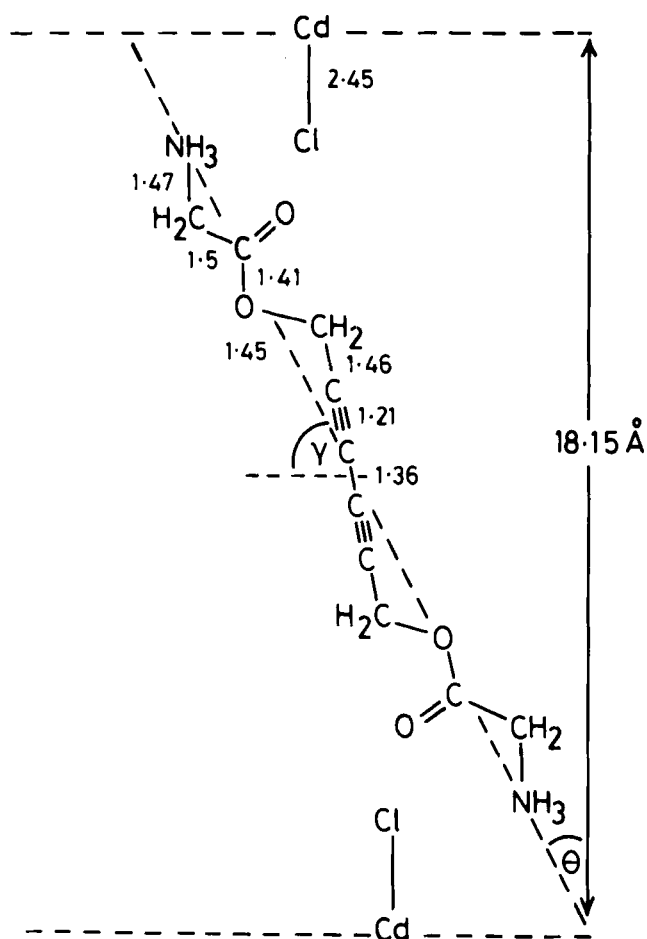


FIGURE 4. Estimated configuration of the diacetylene moiety in  $(\text{H}_2\text{gly-diac})\text{CdCl}_4$ .

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