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- 20. The compound $(rad)_2Mn_2[Cu(opba)]_3(DMSO)_2-2H_2O crystallizes in the monoclinic system, space group$ *Cc*, with*a*= 25.379(8) Å,*b*= 25.146(8) Å,*c* $= 18.845(4) Å, and <math>\beta$ = 131.52(4)°, where the number in parentheses is the error in the last digit, and *V* = 9004 Å³, *Z* = 4, and *d*_{calc} = 1.280 g cm⁻³. Analysis was done at wavelength λ (Mo-K α) = 0.71073 Å. The structure was solved by direct methods and successive Fourier difference syntheses. The refinements by full-matrix least squares gave final *R* = 0.091 and *R*_w = 0.104 from 2642 reflections with intensity *I* ≥ 2 σ (*I*) for 485 variables. Because of the small number of observed reflections, only the Mn and Cu atoms were refined anisotropically. The DMSO and water molecules are disordered.
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Strained-Layer van der Waals Epitaxy in a Langmuir-Blodgett Film

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Atomic force microscope images of Langmuir-Blodgett films of lead and manganese fatty acid salts show that these monolayers have long-range order and are oriented with respect to the mica substrate, although the lattice symmetries of the monolayers and substrate are dramatically different. The surface lattice of sequentially thicker films evolves toward the bulk structure while retaining the substrate alignment. This behavior is in distinct contrast to films of cadmium fatty acid salts on mica, or all films on amorphous silicon oxide, in which the monolayer structure is disordered and a three-layer-thick film displays the bulk structure.

Langmuir-Blodgett (LB) films have been widely studied because of their applications in the areas of molecular electronics, nonlinear optics, cell membrane models, and biosensors (1). Most of the potential applications of LB films are based on the premise of perfect molecular layering and orientation. The technique of atomic force microscopy (AFM) (2), which probes only the outermost layer of the film, is ideal for the study of LB films (3). Although in many ways LB films demonstrate behavior analogous to thin solid films such as having long-range positional order (4-7), grain boundaries (4), and surface reconstructions (6, 7), both interlayer and intralayer interactions in the films can be quite important (6, 7); the presence of these interactions makes LB films relevant to the study of biomembranes, vesicles, and microemulsions.

In the experiments reported here we demonstrate that the growth of certain LB films proceeds by a type of epitaxy which we call "strained-layer van der Waals epitaxy" because it represents a compromise between the well-known strained-layer epitaxy and the recently reported van der Waals epitaxy (8). In contrast with previous work on cadmium arachidate (CdA) (4–6), and barium arachidate (BaA) (7), monolayers of lead stearate (PbSt) on mica substrates have long-range positional and orientational order that differs significantly from both that of multilayer films of PbSt and that of mica.

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However, the lattice is oriented with respect to the substrate. Monolayers of manganese arachidate (MnA) have short-range positional order, but long-range orientational order, and are also oriented with respect to the mica substrate. Monolayers of both materials on amorphous silicon surfaces were completely disordered. These results show that coupling between the substrate and the monolayer and the nature of the counterion have a significant effect on the molecular packing in LB films. The differences between cadmium- and leadcontaining films on mica are all the more surprising given that the structures of thick films (>10 layers) of these materials are nearly identical.

The concept of strained-layer epitaxy is familiar from semiconductor systems. In these systems the first monolayer of an adsorbed film, which has a bulk lattice constant no more than a few percent different from that of the substrate, replicates the in-plane structure of the substrate exactly, and subsequent layers gradually relax to the bulk structure of the adsorbate. For PbSt and MnA films on mica, however, the bulk crystal structure has a significant mismatch with the substrate in both lattice constants and lattice symmetry. We show here that centered-rectangular PbSt monolayers are deposited on the hexagonal mica substrate in a well-defined orientation such that there is a close match between one set of lattice rows of monolayer and substrate. However, the other lattice constants of the monolayer are far from commensurate with the substrate. In spite of this large mismatch, PbSt monolayers have long range positional and orientational order. In this regard, the PbSt monolayers are analogous to films of transition metal dichalcogenides

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such as $MoSe_2$ and $NbSe_2$ on mica substrates (8). In these films, the adsorbed layer is oriented with respect to the substrate and has long-range positional and orientational order, but the adsorbed layer maintains its bulk lattice spacings, which are significantly different than those of the substrate. This type of growth has been termed van der Waals epitaxy and is common to adsorbates and substrates that form bulk layered structures with strong intralayer interactions but weak and nonspecific interlayer interactions (8).

For PbSt, the relative strength of the interlayer and intralayer interactions leads to a well-ordered monolaver structure that is expanded and has a qualitatively different alkane chain packing relative to that in a thick PbSt film. Subsequent layers revert to the thick film type of packing, but the values of the lattice constants relax gradually from bilayer to bilayer toward the bulk values. This behavior is in contrast with LB films of cadmium and barium fatty acid salts, in which the monolayer has a disordered structure that abruptly changes to the bulk packing as an additional bilayer is added (4-7). These results can be explained by the relatively large increase in the strength of the intralayer interactions for PbSt as compared to CdA and BaA as shown by pH, isotherm, surface potential, and surface viscosity and elasticity measurements (9-11). Our results also suggest that better ordering in LB films might be achieved by (i) designing molecules to maximize intralayer interactions while minimizing interlayer interactions (12) and (ii) coupling the LB films to a substrate with similar lattice symmetry.

In our experiments, we spread stearic $(CH_3(CH_2)_{16}COOH)$ or arachidic $(CH_3-(CH_2)_{18}COOH)$ acid from chloroform (1.8

mg/ml) onto an aqueous subphase with 0.5 mM Pb(CH₃COO)₂ or MnCl₂ adjusted to pH 7.0 with NaOH (13). Hydrophilic substrates were mica or the amorphous native oxide on polished silicon wafers (SiO_x) (14). The substrates were prepared as in (15). Isotherms and film deposition were done on a NIMA (16) trough at $22.0^{\circ} \pm$ 0.5°C and a surface pressure of 30 ± 0.1 mN/m. Film transfer was by vertical dipping at ~ 2 mm/min; transfer ratios were approximately unity. We noticed an obvious increase in the surface viscosity and elasticity of PbA relative to CdA or BaA; monolayers of PbA were too rigid to transfer onto the substrates so PbSt was used. The PbSt monolayers were also more rigid than CdA or MnA, but we were able to transfer them satisfactorily. These observations are consistent with more detailed measurements showing that Pb containing films had substantially greater surface elasticity and viscosity than CdA films (10). We performed the AFM measurements with either a Nanoscope II or Nanoscope III FM (17) at ambient temperature, using a 1 μ m by 1 µm scan head and a silicon nitride tip on a cantilever with a spring constant of 0.12 N/m. The best molecular resolution was achieved with the force mode, that is, scanning the tip at constant height and measuring spring deflection. Typical forces were 10^{-8} N.

With the exception of the monolayer on silicon, which gave a disordered surface, reproducible molecular resolution images that were free of drift were obtained on at least two different samples of each type of film. Lattice parameters were obtained for all of these films. Quantitative results are based on statistical analysis of at least six images (30 nm on a side) taken with at least three different AFM



Fig. 1. (**A**) Unprocessed image of a monolayer of PbSt on mica (30 nm by 30 nm). The inset shows the Fourier transform (FT). The numbers are Miller indices (hk) corresponding to the lattice directions. Details of the calibration and analysis in obtaining these images are described elsewhere (4-7). (**B**) Raw image of the underlying mica lattice after the film was cleaved from the substrate (without moving the substrate) with inset showing the FT. Note the similarity in orientation and lattice dimensions of the [02] spot of the monolayer with the indicated spot of the mica (arrowhead).

tips for each sample (a minimum of 18 images per sample). The details of the calibration and analysis are identical to those reported earlier (4-7). To check for epitaxial growth, the one-layer, three-layer, and five-layer films on mica were subsequently cleaved while the sample was mounted on the AFM and imaged without moving the sample. These gave the orientations of the underlying mica lattice (18).

A molecular resolution image of a PbSt monolayer on mica is shown in Fig. 1A with the Fourier transform (FT) inset. The



Fig. 2. (A) Unprocessed image of a monolayer of MnA deposited on mica with the FT inset. Although individual molecular features are visible the image clearly lacks the regularity observed in the case of PbSt. (B) One-dimensional cross sections taken along a lattice direction (when one exists) of the two-dimensional autocorrelation functions. From top to bottom the data correspond to three-layer CdA, one-layer CdA, three-layer MnA, one-layer MnA, threelayer PbSt, and one-layer PbSt. The solid lines, corresponding to the three-layer films, show substantial correlations at 10 nm, as does the dashed line corresponding to the one-layer PbSt film. However, the one-layer MnA has only five or six maxima because of its short-range order, and the one-layer CdA has a correlation length less than the nearest neighbor distance.

underlying mica substrate is shown in Fig. 1B along with its FT. Note the similar orientations of the [02] spot of the monolayer and one of the lattice spots of the mica (as the lattice is hexagonal all mica spots are degenerate). On each of five different samples examined, the [02] direction of the monolayer was aligned with a mica lattice direction within the accuracy of our measurement $(\pm 1^\circ)$ whereas the other two directions were off by 4° to 6°. The best fit lattice we have extracted from the monolayer images is a centered rectangular lattice with a unit cell of two molecules. The unit cell dimensions are a $= 0.447 \pm 0.004$ nm and $b = 0.920 \pm$ 0.006 nm, giving a molecular area of 20.6 \pm 0.4 Å² per molecule. Such a packing (the ratio of $b/a \approx 2$) is not typical of bulk alkane crystals (19); however, a structure with a similar packing has been observed by electron diffraction of an LB monolayer (20). The lattice structure of an MnA monolayer (Fig. 2A) is more difficult to determine as the positional correlations

extend only 3 nm (see Fig. 2B); therefore, the error bars are larger. However, the local packing is similar to that of the PbSt with the rectangular unit cell dimensions $a = 0.46 \pm 0.01$ nm and $b = 0.87 \pm 0.02$ nm. Although the MnA monolayer exhibits only short-range positional correlations, the orientation of the local packing is correlated over at least 100 nm and aligns with the mica substrate in the same way as the PbSt monolayer. This hexatic ordering has been observed before in an LB monolayer by electron diffraction (21).

After we added an additional bilayer of either PbSt or MnA onto their respective monolayers to form three-layer films on mica, the lattice of the trilayers not only shrank but also changed to a more familiar centered rectangular configuration (the ratio of $b/a \approx 1.5$) with a herringbone type of alkane chain packing (4–6) termed the "R" subcell by Kitaigorodskii (19). The lattice constants of a three-layer film of PbSt on mica are 0.514 nm by 0.752 nm. The constants are consistent with an untilted



Fig. 3. (A) Unprocessed image of a three-layer film of lead stearate on mica with inset showing the FT. (B) Corresponding mica lattice obtained after cleavage with FT insert. Note the similarity in orientation between the [11] spot of the LB film and the indicated spot of the substrate.

Table 1. The lattice parameters for a rectangular two-molecule unit cell. *N*, number of layers. The molecular area is given by $(a \cdot b)/2$. The tilt angle is the estimated angle of orientation of the alkane chains from the direction normal to the substrate. Modulation (Mod.) period gives the period of the height modulation, if any (4). Correlation (Corr.) length gives the positional correlation length measured along one of the lattice directions; M, mica; S, silicon; and ?, unknown. Uncertainties for final significant figures are given in parentheses.

Material	N	Sub- strate	Lattice constants		Area	Tilt	Corr.	Mod.
			<i>a</i> (nm)	<i>b</i> (nm)	(Ų)	angle	(nm)	period (nm)
PbSt	1	М	0.447 (6)	0.922 (8)	20.6	0°	>40	None
PbSt	3	M	0.514 (6)	0.752 (8)	19.3	0°	>40	None
PbSt	5	М	0.497 (6)	0.739 (8)	18.4	0°	>40	None
PbSt	7	М	0.493 (6)	0.728 (8)	17.9	0°	>40	None
PbSt	3	S	0.492 (6)	0.728 (8)	17.9	0°	>40	None
PbSt	1	S	None	None	?	?	?	None
MnA	1	M	0.46 (1)	0.87 (2)	20.0	?	~3	None
MnA	3	M	0.495 (6)	0.791 (8)	19.6	19°	>40	1.18 (8)
MnA	5	M	0.481 (10)	0.812 (10)	19.5	19°	>40	1.18 (8)
MnA	3	S	0.477 (6)	0.834 (8)	19.9	19°	>40	1.18 (8)
MnA	1	S	None	None	None	?	0	None

R[00] lattice (19). The orientations of the PbSt lattice and the underlying mica lattice (Fig. 3B) are similar, as shown by the [11] reflection of the LB film (6) and one of the reflections of the mica substrate. The [11] direction of the trilayer was always aligned with that in the mica.

The difference between the monolayer and trilayer films of MnA are more dramatic (Table 1). The MnA trilayer has longrange positional order as well as orientational order. The lattice constants of the three-layer film of MnA (Fig. 4) are consistent with a tilted R[01] lattice in which the alkane chains are tilted by 19° with respect to the surface normal (19). The MnA trilayer also exhibits a long-range undulation superstructure, similar to those observed in multilayer films of CdA but of shorter wavelength (4) (Table 1).

As is clear from Table 1, the films on mica eventually relax to their bulk structure; PbSt relaxes after seven layers and MnA after five layers. PbSt and MnA films deposited on amorphous silicon oxide, however, achieve the structure of a bulk sample after only three layers whereas the monolayer is disordered. The lattice constants of a seven-layer PbSt film on mica and a three-layer PbSt film on SiO_x are in excellent agreement with measurements of close-packed, untilted, aliphatic systems in a herringbone packing (22–26) and are also consistent with x-ray diffraction results from PbSt multilayers (27).

The dramatic difference between monolayers of PbSt, MnA, and CdA (4– 6) or BaA (7) deposited on amorphous silicon oxide and crystalline mica substrates demonstrates the importance of the substrate and counterion on molecular organization of LB films. The PbSt and MnA monolayers are oriented with respect to the substrate, and their lattice structures are significantly different from those



Fig. 4. Unprocessed image of a three-layer film of MnA on mica with inset showing the FT. Additional spots in the FT are due to a periodic height modulation in the film (4).

of a thick film. Each alkyl chain in the films with three or more layers of PbSt or MnA has four nearest neighbors at a relatively close-packed distance of 0.44 to 0.45 nm and two nearest neighbors at a distance of 0.48 to 0.51 nm. However, the alkyl chains in the monolayer films have only two nearest neighbors at a short distance of 0.45 to 0.46 nm and four nearest neighbors at a distance of 0.49 to 0.51 nm (see Fig. 5). This packing is unlike that of the other types of alkane lattices in LB films (4-7), although it may be related to a rectangular arrangement based on the M packing [which Kitaigorodskii (19) rejected because of its low density], which has ideal cell dimensions of $a_1 = 0.42$ nm and $a_2 = 0.91$ nm (19). The nearest neighbor packing in the mica lattice is 0.52 nm, which indicates that the monolayer lattice is most likely expanding to match that of the mica. However, the overall symmetry difference between adsorbate and substrate makes for a rather poor match. Thus these films have chosen a middle ground between strainedlayer epitaxy, in which the monolayer replicates the substrate structure exactly and gradually relaxes to the bulk structure with additional layers, and van der Waals epitaxy (8), in which the epitaxial crystal film takes on its bulk lattice constants even at submonolayer coverage (although the adsorbate lattice constants can be quite different from those of the substrate) but is aligned with respect to the substrate.

Although the lattice structures of the monolayer and multilayers are rectangular, the monolayer lattice is qualitatively different from that of the multilayers. The monolayer lattice, characterized by a b/aratio of about 2, is unusual for bulk aliphatic compounds, but has been seen in an LB monolayer (20) and has the same alkane chain packing as a tilted structure observed by x-ray diffraction in a fatty acid monolayer on an aqueous subphase (28). The subsequent bilayers take on a more familiar type of lattice that is characteristic of the herringbone packing. From the comparison of the multilayer FT with the FT of the underlying mica substrate, we conclude that both the [02] and the [11] directions of the multilayer film are nearly aligned $(<1.5^{\circ})$ with the degenerate [11] and [1T] directions of the monolayer and that the [11] direction of the multilayer is aligned with a mica repeat direction (Fig. 5). The lattice constants of subsequent bilayers gradually relax while maintaining approximately the same b/a ratio until the bulk structure is reached at seven layers. This picture is consistent with earlier x-ray diffraction measurements on thick (100 bilayers) PbSt films on mica (27) in which it was found that the [11] direction



Fig. 5. A schematic overlay of the reciprocal space lattices of mica (filled), a PbSt monolayer (shaded), and a five-layer PbSt film (open). The squares represent the [02] or nondegenerate lattice repeat direction, while the circles represent the degenerate {11} family of repeat directions. The [02] direction of the monolayer (shaded square) is exactly aligned with a mica repeat direction (filled circle). The small arrows point out the close correspondence between the orientation of the [11] direction of the five-layer film and one of the mica lattice directions as was also observed by x-ray diffraction (27).

of the LB film was aligned with a mica repeat direction. Our experiment, in which we followed the growth from layer to layer, provides an explanation for this alignment.

The significant difference in monolayer ordering can be explained by the stronger intralayer interactions for Pb fatty acid salts as opposed to Cd or Ba. Isotherm and surface potential data show that complete binding of Pb ions to fatty acid monolayers is complete by pH 4.5, whereas complete binding of Cd is not achieved until pH 6.5, and for Ba until pH 9 (9, 11). This difference suggests that Pb binds more effectively to the fatty acid headgroup than does Cd or Ba and facilitates condensation of the monolayer (11). Monolayer films of Pb fatty acid salts also show greater surface viscosity and surface elasticity than do Cd fatty acid salts; this difference again suggests that the intralayer interactions are significantly stronger (9, 10). These stronger intralayer interactions in Pb salts likely help hold the monolayer together despite the large mismatch between the fatty acid lattice and the substrate lattice. Our results suggest that the interactions between the Mn fatty acid salts must be intermediate between those of Cd and Pb. The greatest order in LB films should result from optimization of a van der Waals type of epitaxy; ordering in LB films might in general be achieved by designing molecules to maximize intralayer interactions while minimizing interlayer interactions (12) and simultaneously coupling the films to a substrate with similar lattice symmetry.

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