

Table 1 Properties of ionic bis(stilbazole) silver (I) mesogens

Compound	Transition		T (°C)	ΔH (Jg ⁻¹)	ΔS_m (R)
AgL ₂ ⁽³⁾ LS	K	S ₂	147	51.7	11.8
	S ₂	I	159	0.8	0.2
AgL ₂ ⁽⁴⁾ LS	K	S ₂	156	42.7	9.8
	S ₂	I	168	0.7	0.2
AgL ₂ ⁽⁸⁾ LS	K	S ₁	144	40.8	11.4
	S ₁	S ₂	164	3.6	0.9
	S ₂	I	177	1.4	0.4
AgL ₂ ⁽⁸⁾ BF ₄	K	M ₁	170	15.6	3.0
	M ₁	M ₂	270	16.4	2.5
	M ₂	I*	300	10.1	1.5

K, crystal; S, smectic (see text); M, unidentified mesophase; I, isotropic.

* With decomposition.

the 'melting' transition is in contrast with the normal behaviour of anhydrous ionic amphiphiles which show only one such phase, that is the lamellar or neat phase: other more ordered ribbon or disk phases occur below our designated melting transition. Figure 3 gives optical textures for the two high-temperature mesophases. The lower temperature texture is similar to the smectic B texture obtained for the free stilbazole ligands, whereas the higher temperature texture is more typical of a lamellar phase.

The mesophase structures of anhydrous ionic amphiphiles are based on the aggregation of polar head groups, where the charges are cancelled by counter ions (Fig. 1). Measurements of the order parameters of alkyl chain segments indicate²² that the orientational order is low compared with thermotropic liquid crystals. The new ionic liquid crystals reported here have anisotropic rigid cores that may be expected to enhance the

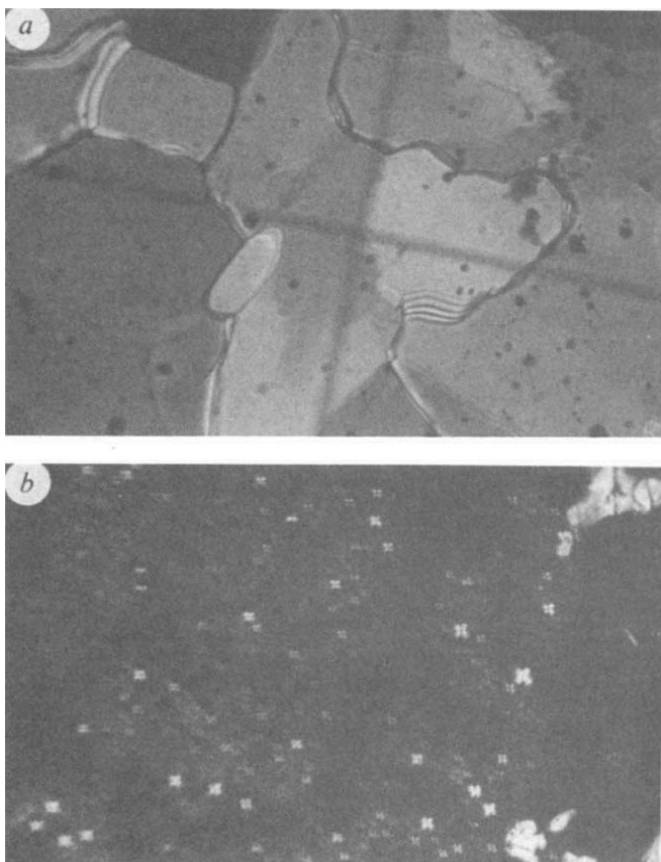


Fig. 3 Optical textures for two high-temperature phases of [AgL₂⁽⁸⁾][LS]. *a*, 148 °C: S, smectic B; *b*, 176 °C: S₂, lamellar.

orientational order and hence the macroscopic anisotropy of the mesophases. At present, we have no information on the packing of anions and cations in the mesophases, but we might expect oppositely charged ions to interact in a manner similar to that shown in Fig. 1. The combination of thermotropic and amphiphilic phase properties in a single system has interesting consequences. For example the anisotropy of the rigid part of the mesogenic ions may ease the external control of macroscopic orientation by applied fields. In conventional Langmuir-Blodgett (LB) films, orientational order is achieved by surface packing of the polar head groups. By incorporating strongly anisotropic groups into the polar part of the molecule, it may be possible to produce orientationally ordered LB films more easily, and with larger macroscopic anisotropies. The effect of solvents on these mixed ionic liquid crystals has not been investigated, but may be expected to lead to a rich phase behaviour.

We are currently investigating mesophase formation between organic mesogenic anions and cations²³. The metal-containing cation in the materials described above may be replaced by an organic cation for example quaternary N-containing system, and these materials when combined with mesogenic anions also exhibit a rich mesophase behaviour.

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Sulphur-induced faceting of platinum catalyst particles

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The poisoning of metal catalysts by sulphur is a serious problem in many chemical processes, but in some cases partial poisoning can produce beneficial changes in catalytic selectivity^{1,2}. The mechanism whereby adsorbed sulphur affects selectivity has been the subject of much debate; one view³ is that during poisoning a restructuring of the metal surface occurs that alters the activity of the catalyst towards structure-sensitive reactions. The adsorption of sulphur can induce 'faceting' of macroscopic metal surfaces (see for example ref. 4), so a similar phenomenon might occur when sulphur interacts with the small supported metal particles which are used in practical catalysts. Here I show, using transmission electron microscopy, that sulphur adsorption can produce a transformation in the morphology of alumina-supported

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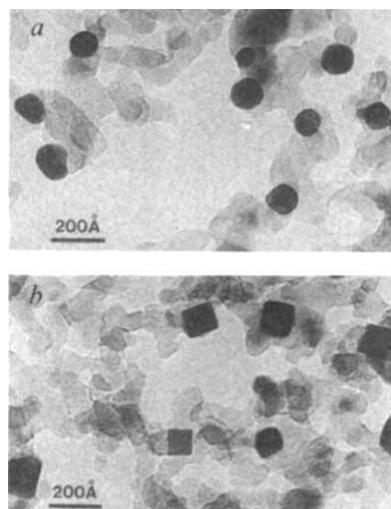


Fig. 1 Micrographs illustrating change in platinum particle morphology induced by sulphur adsorption. *a*, Specimen heated in air at 700 °C for 1 h. *b*, Specimen heated in flowing H₂S/H₂ at 500 °C for 16 h, following a similar air heat-treatment. Scale bar, 200 Å.

platinum particles, which apparently involves the formation of sharp (100) facets. This supports the restructuring model of sulphur poisoning³, and suggests that more attention should be paid to the role of adsorbate-induced faceting in the poisoning and promotion of supported metal catalysts.

The specimens used in this study were prepared by a novel technique which enables thin self-supporting catalyst films to be prepared directly on stainless-steel microscope grids. The technique, which is based on a process for applying catalytic coatings onto metallic or ceramic substrates, involved dipping the grids into an aqueous alumina sol to which a solution of tetrammine platinum (II) chloride had been added, drying the resultant film to a gel and then firing and reducing this to form thin sheets of platinum/alumina^{5,6}. Before carrying out the sulphur poisoning experiments, the freshly prepared specimens were heated in air at 700 °C for 1 h to increase the mean platinum particle size from 50 to 113 Å. This was necessary because the precise nature of sulphur-induced changes in particle morphology proved difficult to identify when fresh specimens were used. The air-sintered specimens were then placed in a controlled atmosphere furnace and a mixture containing 100 v.p.m. (volumes per million) hydrogen sulphide in hydrogen was passed through at a flow-rate of 30 cm³ min⁻¹. After flushing for 30 min at room temperature the specimens were heated to 500 °C over a period of 1 h, maintained at this temperature for 16 h and then allowed to cool. In these conditions, elemental sulphur would be expected to deposit onto the platinum particles, but formation of bulk sulphide would be unlikely^{1,2}. Specimens were examined using a JEOL 200CX transmission electron microscope operated in bright-field mode with an accelerating voltage of 200 kV.

Figure 1 shows micrographs of typical regions of unpoisoned and poisoned catalysts, while Fig. 2 shows the most commonly observed particle shapes before and after poisoning. Platinum particles in the unpoisoned catalysts were generally well rounded (Fig. 1*a*), with only slight faceting and no sharp edges or corners. Most particles were single crystals, and although many of these were irregular in shape, a significant proportion could be identified as rounded octahedra, indicating a degree of (111) faceting. Figure 2*a* shows a typical example of such a particle. The change in morphology induced by poisoning can be seen clearly in Fig. 1*b*. Instead of slight (111) faceting, single crystal particles in the poisoned catalyst exhibited predominantly square profiles strongly indicative of (100) faceting. Figure 2*b* shows another typical single crystal in a poisoned catalyst. The type of contrast

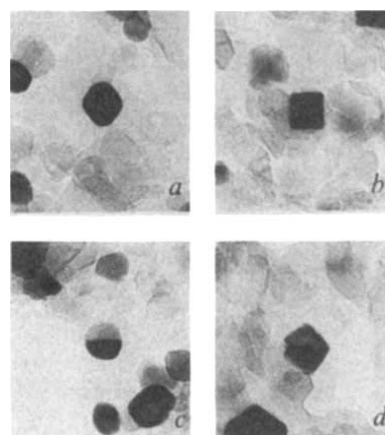


Fig. 2 Typical particle structures in unpoisoned and poisoned catalysts. *a*, Single crystal particle in air-heated specimen (rounded octahedron). *b*, Single crystal in sulphur-treated specimen. *c*, Twinned particle in air-heated specimen. *d*, Twinned particle in sulphur-treated specimen. Scale bar, 200 Å.

exhibited by these particles showed them to be three dimensional rather than 'raft-like' in form, indicating that their overall shapes were approximately cubic. In some cases, the (100) faceting was almost perfect with very little rounding of the corners visible, even at the highest magnification. The morphology of particles containing a single twin boundary was also transformed by sulphur adsorption. In the air-heated catalyst, such particles were often roughly circular in outline (Fig. 2*c*), while after poisoning they frequently exhibited the faceted profile shown in Fig. 2*d*. This profile is again indicative of (100) faceting and suggests an overall shape of the type sketched in Fig. 3.

To confirm that the observed changes in particle morphology were due to sulphur adsorption, a control experiment was carried out which involved heating catalyst specimens in pure hydrogen in conditions identical to those used in the hydrogen sulphide/hydrogen treatments. This resulted in relatively little change in particle shape, but the degree of faceting appeared to decrease slightly producing particles with almost circular profiles.

The observations reported here are consistent with studies of macroscopic metal surfaces. For example, Schmidt and Luss⁴ have shown that treatment of platinum/rhodium gauzes with hydrogen sulphide results in the formation of (100) surface planes, while McCarroll *et al.*⁷ report a "reorientation" of the (111) face of nickel to (100) in the presence of hydrogen sulphide. However, sulphur-induced faceting has not previously been observed directly using specimens which closely resemble real supported catalysts. Indeed, the effect of adsorption on the surface structure of very small metal particles has received surprisingly little attention. *In situ* transmission electron microscopy work⁸⁻¹⁰ has indicated that the shape of very small noble metal particles can be changed by exposure to oxygen, carbon monoxide and other gases, although these results were partly

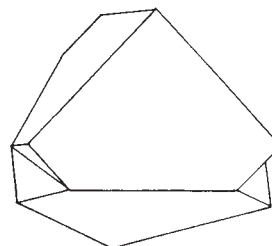


Fig. 3 Shape of twinned particle bounded by (100) facets.

explained in terms of changes in the particle-support interaction. Gillet *et al.*^{11,12} have reported changes in the morphology of palladium particles induced by carbon monoxide/oxygen mixtures, while Wang *et al.*¹³ have found that platinum particles develop (100) facets when heated in hydrogen, in contrast to the findings of this study. Previous work¹⁴ has shown that heating platinum/alumina specimens in a vacuum furnace induces the formation of strong, mainly (111), facets. This was attributed to the deposition of carbon onto the surfaces of the particles during heat treatment in the relatively poor vacuum. Lamber and Romanowski^{15,16} have made a similar observation but again they interpret their results in terms of a metal-support interaction. Further studies of the type described here are required if a more fundamental understanding of the factors which control the structure and activity of supported metal catalysts is to be gained.

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Role of plutonism in low-pressure metamorphic belt formation

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Wickham and Oxburgh¹ recently proposed that low-pressure/high-temperature (low-*P*/high-*T*) metamorphism in the eastern Pyrenees, and possibly all low-*P*/high-*T* metamorphic belts, resulted from anomalously high mantle heat flow brought about by rifting. Their model is largely constrained by the presence of nearby synmetamorphic rift-related sedimentary rocks and the interpretation that the migmatites and granites are the product of *in situ* melting in the presence of an anomalously steep geotherm. Here we present an alternative model, in which low-*P*/high-*T* metamorphism (pro-grade reactions at pressures near or below the Al₂SiO₅ triple point) results from contact effects near sill-like igneous intrusions at intermediate crustal levels. Low-*P*/high-*T* conditions can be achieved through this process in regions of continent–continent collision with normal mantle heat flux as well as in zones of extension. Our model is based on studies of the low-*P*/high-*T* metamorphic terrane in the New England Appalachians.

Regional metamorphism in zones of continent–continent collision can be modelled mathematically as a thermal consequence of large-scale crustal thickening and subsequent erosion^{2–5}. Such models depend on a previous knowledge of the burial and erosion history of the region. In addition, it is assumed that crustal radioactivity and a constant mantle heat flux are the only heat sources and that conduction is the only mode of heat

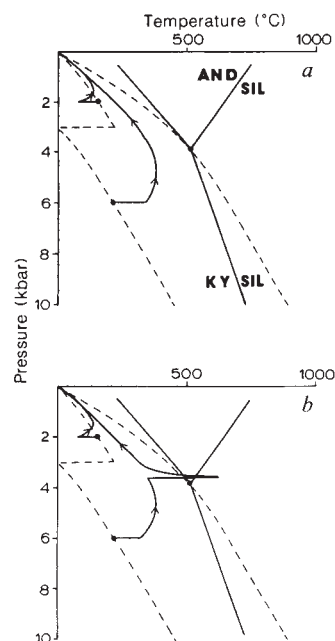


Fig. 1 Hypothetical *P*-*T*-*t* paths after instantaneous thrusting of a 12-km slab, projected onto the pressure-temperature plane. The dashed line to the left is the temperature distribution immediately after thrusting; that to the right is the equilibrium temperature distribution that would result if no erosion was to occur. Solid curves give the time evolution of the temperature for crustal horizons in the upper and lower plates when a period of quiescence proceeds erosion and *a*, magmatic intrusions are ignored, *b*, a magmatic intrusion in the lower plate is considered. Mantle heat flux is 37 mW m⁻². Radioactive heat production of 4.2 mW m⁻³ is uniformly distributed throughout the upper plate and the top 7 km of the lower plate. The aluminosilicate triple point is after ref. 35.

transfer. Although the pressure-temperature-time (*P*-*T*-*t*) path followed by a particular crustal horizon is a function of many parameters, two important generalizations can be made. (1) Melting in the lower crust can be a consequence of crustal thickening. (2) *P*-*T*-*t* trajectories only pass through both the sillimanite (SIL) and the andalusite (AND) stability fields in models with extreme values of the thermal conductivity, mantle heat flux or radioactive heat production in the crust. Moreover, they do so with retrograde metamorphic conditions. Prograde AND to SIL reactions are not predicted (see Fig. 1*a*).

For Barrovian metamorphic terranes, these mathematical models yield results that are consistent with the geological observations^{2,3,5}. However, they fail to predict the prograde AND to SIL metamorphism that is characteristic of many low-*P*/high-*T* belts^{6,7}. Hence, conduction in a tectonically thickened crust with a constant mantle heat flux does not account for the main feature of many low-pressure metamorphic belts. Therefore, we suggest that granitoid magmas produced in the lower crust in response to crustal thickening may be emplaced at intermediate levels, causing deep-level contact effects with low-*P*/high-*T* mineral assemblages. Such crustally-derived plutons are abundant in many low-*P*/high-*T* belts^{6,7}. Qualitatively, the thermal effect of a magmatic intrusion is to increase rapidly and isobarically the temperature of the adjacent country rock (Fig. 1*b*). As will be shown below, in regions of the thickened crust, prograde AND to SIL metamorphism can be produced by this mechanism assuming normal mantle heat flux. Wickham and Oxburgh¹ proposed a different mechanism. They suggested that anomalously high mantle heat flux and convection through mafic magmas from the mantle initiated by lithospheric extension would lead to the formation of low-*P*/high-*T* assemblages. The granitoid plutons which are abundant in many low-*P*/high-*T* belts are interpreted by them to be a result of *in situ* melting.