

## Q1

23 scripts

average 13.01, which ranged from 5.75 to 18

There was a rather wide range of answers for part (a), and problems polymerising several of the monomers were discussed directly in the lectures (1, 3, 4 and 5). Most students were able to readily calculate the DP of the parent polymer in part (b), however, it was a challenge for several students to calculate the number of cleavages and hence the H-t-T and H-t-H linkages. Some students struggled to draw both monomers and the polymer but most were able to calculate the PDI correctly in part (c). Finally, almost everyone answered part (d) correctly, which was directly discussed in the course.

## Question 2

A relatively straightforward question involving x-ray powder diffraction and routine x-ray emission spectroscopy. For part (a), almost all candidates had no difficulty in stating the main advantages of powder diffraction methods, although a few did not appear to be aware that the high peak intensities imply high accuracy in structural refinement. All candidates bar one had no problems indexing the powder pattern in (b) and determining the unit cell content, and most used the experimental structure factor ratio to determine the fraction of cation sites occupied and hence the valence of the iron atoms. However, only a handful of candidates pointed out that this was only valid if the cation vacancies were distributed at random. For part (c), all managed to determine the doubled unit cell and all but one or two could prove that the effective particle size had decreased by some 90%. Part (d) however, caused several problems, as although all candidates were aware that measurements with a low FeL/FeK $\alpha$  intensity ratio should be eliminated from the analysis, few appeared to realise exactly why this should be done. Although most candidates correctly described the larger unit cell as being due to ordering, only a few specified that this was probably due to regularising the Fe<sup>2+</sup>/Fe<sup>3+</sup> arrangement, and only one or two correctly deduced that the new phase was Fe<sub>3</sub>O<sub>4</sub>.

**No. of Attempts: 20 Average mark : 13.45**

## Q3

This question was attempted by 25 candidates and the mean mark was 6.5.

The first part was generally fine though a few candidates suggested incorrect aggregation states for the 'ate complexes. The complexes featured in the handouts.

Part ii proved difficult to the vast majority of candidates. Surprisingly few mentioned the idea of the trimer ring needing to pucker in order for stacking to work. The lecture notes explicitly cover this – puckering allowing electron density to project vertically (hence, less puckering for oxygen rings on account of the additional lone pairs). Instead, many candidates just discussed angles as a function of hybridization at N or O.

Part iii was very well done. Of the very few incorrect answers supplied, incorrectly suggesting lithiation adjacent to O was the most common problem.

(b)

(i) Why is  $\text{GaCl}_2$  diamagnetic?

*This was a simple question involving straight recall of notes from the lecture course and was also covered in 1A (a mixed  $\text{Ga}^I\text{Ga}^{\text{III}}$  salt). Nevertheless, not many candidates managed to give the correct answer with many not even knowing the number of valence electrons on Ga.*

(ii)  $\text{GaCl}_2$  dissolves in benzene. What species is formed and why is  $\text{CaCl}_2$  insoluble in benzene whereas  $\text{GaCl}_2$  is soluble?

*To answer fully, candidates would have needed to know  $\text{GaCl}_2$  was a mixed  $\text{Ga}^I\text{Ga}^{\text{III}}$  salt with only  $\text{Ga}^I$  interacting with benzene. Few gave the correct structure which is quite complex but most marks could be gained by showing hard  $\text{Ga}^{\text{III}}\text{-Cl}$  and softer  $\text{Ga}^I\text{-benzene}$  interactions. Several more students were given credit for knowing  $\text{CaCl}_2$  was purely ionic and  $\text{GaCl}_2$  involved covalent interactions with the solvent.*

(iii) What kinds of products are formed when  $\text{GaCl}_2$  is dissolved in donor solvents? How are these useful starting materials for the preparation of a range of Ga organometallics?

(iv) What other synthetic route could be used to access these types of organometallics?

*These were answered very well, generally, as these synthetic routes were stressed quite strongly in the lectures. Some alternative routes which were not covered in lectures were also proposed were also given credit if they were chemically sensible (for example partial replacement of halides by carbon).*

(v) What would be the result of a one electron reduction of these organometallics? What experimental techniques could be used to probe this change? (Ga abundance: 60%  $^{69}\text{Ga}$ ,  $I = 3/2$ ; 40%  $^{71}\text{Ga}$ ,  $I = 3/2$ ).

*A more difficult section was given as the final part of the question to differentiate the strongest candidates. Many recognised there would be an increase in bond order but most did not state that X-ray diffraction could be used to detect bond length. Even though the question stated a one electron reduction, not many students recognised the product would be a free radical having an unpaired electron. Fewer still mentioned EPR spectroscopy as an experimental technique and only one successfully calculated the expected splitting pattern.*

*Approximate division of marks: (b): (i) 5%, (ii) 10%, (iii) 10%, (iv) 5%, (v) 20%.*

**Q 5a (paper 1)** 29 answers. This was reasonably well answered, although a good few candidates did not properly use the Lewis acid in their mechanistic interpretation. Almost all candidates identified the first intramolecular Diels-Alder reaction as involving an endo mode to set the stereochemistry, but several failed to show convincing 3D transition state representations. In the second step, some candidates incorrectly suggested an ionic mechanism involving electrophilic attack on the furan. The final aromatisation step proved testing to several candidates who did not invoke the Lewis acid at all. Overall, this question tested the manipulation of complex structures in 3D, mechanistic reasoning and stereochemical aspects.

Q5 (b), M5

Generally done well, except many answers did not comment on the imine formation selectivity and the relative stereochemistry of the final step. A 3D picture is needed to show the thermodynamic advantage of cis over trans, and a comment on the anomeric effect.

**Q.7 (course M7 Solid Electrolytes) paper 1**

Marks/20: 18, 18, 17, 14, 14, 13.5, 13, 11, 10.5, 10, 5

Mean mark = 13.09

(a) Part (a) was a straightforward piece of bookwork and the majority of the candidates answered this part successfully. Some of the candidates forgot to mention about the tilt in the potential-energy landscape bringing a bias in the direction of diffusional jumps.  
 (b) This part assumed an extension of dimensional analysis from 1d (discussed in the lectures) to 3d. This part was answered well by the majority of the candidates. Some students forgot to define the quantities given in the formulation of the question.

(c) The first part of the question was straightforward bookwork which most candidates correctly answered. Only a few candidates correctly differentiated between ion trapping and electron scattering as the causes of a steady-state drift velocity under the action of an applied electrical field. A somewhat greater number of candidates correctly identified that the dominant temperature dependence in the case of ionic transport comes from the Arrhenius temperature dependence of the mobility/diffusion constant, with the  $1/T$  term having only a slight effect.

#### Q8

There were 16 people who took this question and overall this was answered well. The second part (Part b) of the question was set by Dr Gonçalo Bernades. Part (a) had two parts (i) and (ii). The first part (i) had three questions and these were taken directly from the lecture notes. These questions were answered well however in some cases only partial answers were given where further elaboration was needed. The second part (ii) of the question involved extending beyond what was given in the lecture course. This was answered well however again in some cases these were only partially answered and needed further elaboration. In all cases the question was answered suggesting that there was sufficient time allocated.

#### Q 8 – b (i, ii)

Generally answered well. Average mark – 7.04 out of 10 marks – half of the total of the question.

- (i) This was generally well answered by the students including mechanist details.
- (ii) While many student were able to identify that the placement of a basic group next to the maleimide can promote faster hydrolysis, some difficulties were found when drawing the structures and mechanism.

Q9:

Candidates generally gave an adequate short discussion on the functioning of single molecule magnets. Most also gave good interpretations of the magnetic susceptibility data for the two manganese compounds although some tried to add the individual spins together before calculating their susceptibility; an approach totally doomed and contrary to what was done in the lectures and workshops. All candidates could write down a spin Hamiltonian for the molecule and most could use it to derive an expression for the energies. Surprisingly few were able to complete the Kambé vector coupling approach to derive the energies of all the possible magnetic states.

Q10

First part was mixed, with relatively few correctly getting all aspects of stereocontrol in the question, as there were a number of factors to consider. Second part was generally quite well done with most candidates seeing the Sonogashira and Pauson-Khand as the key reactions. Average mark – 13.5

Q11(b) - 31 scripts

Average mark 6.34/10

Very wide variety of syntheses proposed including several where little time had clearly been spent on this part. There was a disappointing lack of consideration for chemoselectivity issues (which were explicitly highlighted in the question) given that the route was 3/4 steps in most ways of thinking about the problem. In particular, reagents incompatible with the ester moiety were proposed and the use of an N-oxide as from the lecture notes for the 6-position functionalisation was only exploited by about half the candidates. The use of lithiating reagents was more common than hoped without consideration of their compatibility with other moieties.

Q13:

This question was answered reasonably well. Although the average mark of 12.5 (over 14 scripts) was slightly below the target mark, this was mainly due to a few particularly low marks (5, 6 and 8) while the remaining 11 candidates gained marks ranging between 11 and 18. Parts (a) and (b) involved bond- and electron-counting for the (110) surface of GaAs, and most candidates handled this pretty well. Parts (c) and (d) introduced a more challenging situation involving the reconstructed (001) surface of GaAs, and although many candidates succeeded in identifying all the dangling bonds, most failed correctly to count the number of electrons in them (likely not realising the significance that there were some As-As bonds, in addition to the Ga-As bonds). Part (e) on the Bi-terminated (111) surface of Si was generally handled well, and Part (f) was more-or-less inviting a precis of the notes and again resulted in good marks. Overall, most candidates showed that they understood the principles involved, even if some slipped up on the details.

Q14

This question was very well answered by all four candidates, who demonstrated a good understanding of classical rate theory and its relation to classical transition-state theory. All candidates scored full marks for part (a)(i), and gave good answers to (a)(ii) with extra marks being given for the most general derivation that the rate is independent of the dividing surface. Part (b) on transition-state

theory was also well answered, although no candidate picked up on the fact that a multi-dimensional system could become trapped between two barriers, causing transition-state theory to break down.

Q15: Most who attempted the question remembered from the lectures the 5-membered structure of a cyanostar. Those who got the structure broadly right but the wrong number of monomer units were not penalised beyond 15a. Most gave reasonable answers for the chloride vs PF<sub>6</sub> binding, and many got the rotaxane formation right (some penalty for stating that only one ring threaded as opposed to 2). Only two received full marks for the topological chirality question 15d, however, which required subtle analysis - many received partial marks, however.

Q16: The answers overall were satisfactory although with few really stellar efforts. While parts (a) and (b) were fairly routine it was interesting to see how the distinction between a cocrystal and solvate was frequently confused in terms of definition and indeed how each might actually be prepared. Part (c) was very similar to material in the lectures and here I hoped that I might have a clear indication of how the template molecules controlled the separation of the acetylenes via a non-covalent interaction and might be separated between a di and tri-acetylene monomer. Few actually dealt with this in a fully satisfactory way. Part (d) had the issue (intended!) of referring to a solution of precise stoichiometry to see if the distinction between a cocrystal and solid solution was made clear. In some cases this was and in particular the point about conformational control by structural mimicry was made in several good answers.

Average mark: 12.75. 16 attempts

Question 17

Answers = 31

Average mark = 16.90

SD = 4.46

Min mark = 7

Max mark = 25

The question was well answered by most candidates. Part (a) asked for the PLP mediated mechanism of gamma-aminobutyrate amino transferase. This was similar to transformations that they had seen before, and so almost every answer started on the right lines. The problems that the students seemed to have were not remembering the structure of PMP. Part (b) involved the mechanism of the suicide inhibitor, and it was pleasing to see so many excellent attempts to work out the covalent inhibition involved, although there were only a few who managed to see an aromatic product was possible. Part (c) asked for the FMN<sub>2</sub> mediated mechanism to give chorismate, and was more variable in answers. Pleasingly many answers used variations of SET and H-atom abstraction to get the required product.

**Q. 18**

Answered by 14 candidates, almost all of whom found the question pretty easy. As a result the answers had to be marked quite harshly. Much of the required answer had been given in the notes and therefore answers that were plausible but not the true biosynthetic pathway were marked down. Even so the average came out a little high at 13.96 out of 20.

**Q19**

9 scripts

average of 14.5, which ranged from 7.75 to 19.75 (I tried to remark this several times)

This question appeared to be more difficult than Q20 for the students. In part (a) most students were able to identify correctly the location for controlled free radical polymerisation and anionic ring opening polymerisation, fewer were able to identify cationic ring opening through the oxazoline moiety and very few anionic polymerisation site. Part (b) did not present too many problems as it was directly seen before in the handout questions during the course (even so, quite a few people missed this!). Parts (c) and (d) were more challenging for the students. Many seemed to forget that secondary alkyl amines are capable of also ring opening the monomer in part (c) and everyone missed the obvious clue from part (a) that monomer B was an oxazoline!

**Q20**

21 scripts

average of 20.2, which ranged from 14 to 25 (I tried to remark this several times)

In general the students found this question much more straightforward. Nearly all students correctly described the Trommsdorff-Norrish (gel) effect, part (b). Parts (e) and (f) were answered very well by most students, with a few making silly mathematical errors. While part (d) was directly from the lecture notes, several students did not remember to illustrate the equilibrium between active and dormant chains.

**Q21**

This was a more difficult question involving tetragonal lanthanum-nickel oxide phases. Part (a) was relatively straightforward and generally very well answered, although one or two candidates evidently did not appreciate the advantages conveyed by the scattering from a point nucleus. Part (b) was a standard indexing problem which most had no difficulties with. All appreciated that the first peak was (002) but a few then made the false assumption that the second was (110) and consequently failed to get the correct unit cell. For part (c) all had no difficulty in determining that the new lattice was a primitive unit cell, but not all deduced the reason for the nonequivalence of the two nickel atoms, despite being given the hint that the intensities of the new

peaks fell off rapidly with  $2\theta$ , typical of scattering by unpaired electrons. As with question 2, part (d) caused the most problems. Again many seemed unsure of the real effects of x-ray absorption, and in this more complex question it frequently caused an incorrect grouping of the results. About half of the answers correctly found the presence of  $\text{La}_3\text{Ni}_2\text{O}_7$ , but only three identified  $\text{La}_4\text{Ni}_3\text{O}_{10}$  as a third phase, and just one concluded that the sample also contained the perovskite phase  $\text{LaNiO}_3$ , corresponding to  $n = \infty$  in the series of phases given. Overall though, this question was well answered.

**No. of Attempts: 18 Average mark : 16.94**

### Q22

Answers to this question were a bit disappointing. Nearly all candidates had few problems with part (a) and correctly stated that the main advantage of high resolution electron microscope was in investigating the structures of non-periodic specimens. Answers to part (b) were also, in general good, although some candidates clearly were unsure of the way in which pairs of terms in the intensity series could be taken together to eliminate sine terms from the intensity equation. The role of the power spectrum also caused no problems, although two candidates went into far more detail in describing the determination of  $\chi(S)$  than was necessary. Part (c) was the downfall of most candidates, in that almost invariably they assumed that all the maxima corresponded to a value of  $\sin(\chi(S))$  of unity, whereas at the unique turning point in the curve (i.e where  $\Delta F = C_s \lambda^2 |S|$ ) this is not necessarily the case, and indeed it is not in the diffractogram illustrated. Consequently they did not derive the correct assumption, which was that the defocus value lay somewhere between the Gaussian focus and the so-called Scherzer focus. For part (d), all appreciated that the cause of the damping envelope lay in fluctuations in the defocus value, although not all seemed completely sure of all three reasons for this. However, all candidates correctly derived the comparable resolution limit for  $\text{CuK}\alpha$  X-rays. Part (e) was also a bit disappointing, in that although all understood that these maxima in the power spectrum were the result of mutual interference of diffracted beams, only a few could explain why these could be unaffected by both spherical and chromatic aberration.

No. of Attempts : 14

Average mark : 16.14

### Q23

This question was attempted by 18 candidates and the mean mark was 16.7.

The first part of this question was generally well done given that it was not material directly lifted from the notes. The majority of candidates saw that the aggregates should be tetramers (even if they knew from the notes that **D** could be a tetramer or a hexamer in practice, they correctly saw that **E** should be a tetramer). Most saw the relevance of the  $\text{sp}^2$  carbon to the ability or not of a 4-membered chelate ring to form.

Part ii was very well done. Most candidates correctly spotted that the lithium amide could neither stack nor ladder. The most common fault was predicting an intercepted ladder (tetramer), although the dimeric complex was (in all essentials) featured in the notes. The interpretation of the solution data was done very well – in particular rationalizing the low concentration data.

Part iii proved much more difficult. Most candidates identified **F** correctly though only about half got **G** and hardly anyone got **H** (though the compounds feature explicitly in the notes). The majority of candidates attributed the IR data to a C=N bond – many didn't include Cu in **G**. NMR data was generally attributed correctly. Only the very highest scoring candidates could suggest in other than a very vague way why the amount of THF altered the nature of the products. Presumably this was because so few candidates identified **H**, meaning that very few candidates saw that LiCN (the difference between **G** and **H**) is a compound in its own right.

## Q24

Answer all parts of the question.

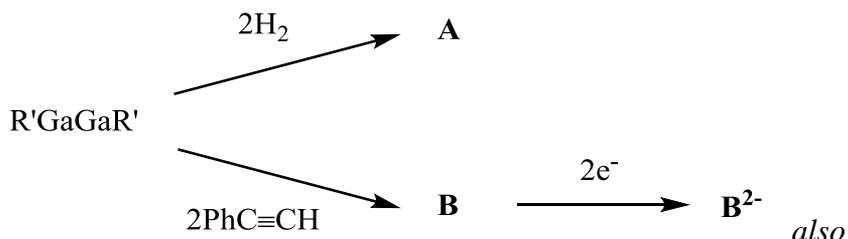
- (a) Discuss the range of structures and any metal-metal bonding found in neutral group 13 organometallic derivatives  $[M^I R]_n$  ( $R =$  carbon ligand) in the solid state. How is the bonding affected by the metal and the nature of the organic ligands?

*This was the straightforward part of the question that simply related to a recall of the material presented in the lectures and notes. There was a very wide spread in the quality of answers presented by candidates and in fact this first part contributed most to the differentiation between candidates' marks.*

- (b) Describe a possible bonding scheme for the dimer  $R'GaGaR'$  ( $R' =$  bulky aryl group) which has a *trans*-bent geometry. What is the maximum possible  $Ga \cdots Ga$  bond order? The  $Ga \cdots Ga$  bond in  $R'GaGaR'$  is weak and it dissociates easily into  $R'Ga$  monomers in solution whereas the reduced form  $Na_2[R'GaGaR']$  is more strongly bonded. What explanations could account for this difference in behaviour? Illustrate your answers with valence bond diagrams.

*Part (b) asked to provide a bonding model to an unfamiliar situation. The concept of the inert pair needed to be understood as well as choosing an appropriate hybridisation scheme for the metal atoms in question. This part of the question was answered well by nearly all candidates who successfully predicted bond orders. The strongest candidates could also explain the weakness of the metal-metal bonds as a result of the inert pair effect.*

- (c) R'GaGaR' reacts readily with two equivalents of hydrogen to give complex **A** or with two equivalents of phenylacetylene to give compound **B** which can be reduced by a two electrons to form **B<sup>2-</sup>**. Suggest structures and bonding in **A** and **B** and explain the stability of **B<sup>2-</sup>**.



Part (c) was

answered well, generally. There was some ambiguity in the stoichiometry in route A. Even though in the scheme it was clearly shown as two equivalents of H<sub>2</sub>, the wording said two equivalents of hydrogen (dihydrogen or hydrogen gas would have been clearer) therefore some students only used one equivalent of H<sub>2</sub> which was also accepted provided the expected product was chemically sensible. Extra credit was given to those who could predict the electron-deficient hydrogen-bridged product. Most candidates also predicted the correct products in route B with the two electron reduction providing a big clue to the cyclic aromatic nature of the final product.

- (d) Suggest products **C** and **D** for the following reactions and explain the reactivity.



The final part of the question was designed to be open and challenging, but very few students even attempted answering it so in hindsight more information should be provided in future questions of this type. Credit was given to those who predicted that the highly unstable Al(I) would become oxidised to Al(III) but only two successfully predicted adamantane and cubane-type structures respectively.

**Q 27 (paper 2)** 27 answers. This question was generally well done, although part (c) intentionally proved testing in the creative design of multi-step stereocontrolled

transformations, leading to a large spread of marks. Parts (a) and (b) were tackled well, although a few candidates were not able to provide viable conditions for reductive removal of the dithiane. In part (c), most candidates were able to outline a reasonable flow chart of what was required in terms of carbon-carbon bond formation but did not propose reliable reagent-based methods for achieving efficient levels of stereocontrol. While the actual route accomplished by Smith (Evans alkylation, Brown allylation) was not suggested, there were some answers with potentially viable alternatives based on enolate chemistry. In part (d), most candidates provided a convincing mechanism and rationalisation for the stereocontrol; while a handful of erroneous answers involved the Wittig olefination step in the middle of the rearrangement to generate the tetrahydropyran ring. Overall, this question served to test both the background knowledge and creative ability of the candidates.

Q28, M5

The function of HMPA was missed by many, despite being mentioned in the lectures; confidence in the Woodward Hoffmann rule seemed slightly shakey at times; acetal formation was found challenging in a surprising number of scripts. Overall, however, a complex question was tackled well, and many good answers were produced.

### Q30

#### Candidate X

There was a relatively minor inaccuracy in part (a), while part (b) was carried out satisfactorily.

#### Candidate Y

The answer in part (a) was correct, but the procedure was not clear. Part (b) was carried out satisfactorily, but more details and comments would have been welcomed.

### Q 31 (M7)

- a) Very straightforward – all answers correct.
- b) (i) all answers correct, but for (ii) several candidates did not recognise that holes could be trapped by interstitial ions with decreasing temperature.
- c) All candidates successfully obtained the correct expression for the concentration of holes from the equilibrium constant for the defect reaction. However, very few correctly managed to obtain the correct expression for the conductivity activation energy (being half the enthalpy change of the defect reaction) since they did not recognise that this came from the temperature dependence of the equilibrium constant.
- d) Most candidates correctly identified the four possible defect reactions involved in the aliovalent doping.

- e) However, few then correctly identified the probable behaviour of all the aliovalent dopants involved.
- f) And fewer still then specified the correct likely influence of the effect of such doping on the ionic conduction of *specific* ions.

Q.32, M7 - Solid electrolytes, paper 2

Marks/25: 25, 24, 20.5, 6  
Mean mark = 18.9

All the parts of the question were based on the exact formula for diffusion coefficient in 1d which has been derived in lectures.  
Practically all the candidates successfully attempted the question. A typical drawback was to use the virtual crystal approximation in part (c), although 50% of marks available for this part were given in such cases.

Q 33

Generally answered quite well. Average mark – 16.90 out of 25 marks.

a.

- (i) Almost all students were able to answer this question in very good detail.
- (ii) While the inverse electron demand Diels-Alder mechanism was well understood and students could draw the mechanism, in most cases they did not provide a good explanation of the different requirements compared to the conventional Diels-Alder.
- (iii) Almost all students failed to provide a detailed mechanism for the decaging reaction although they suggested the right product formation.

b.

- (i) This was understood and well explained by almost all students.
- (ii) Students provided a satisfactory explanation of how the molecules enter cells, and only some were able to explain where in the cell the drug would be released from the carrier.
- (iii) Nearly half of the students could show exactly the mechanism with some only providing a diagram for half the steps.

Q34

There were 14 people who took this question and overall this was answered well. There were a number of different sections to the question ranging from material to which has been given out to accompany the lectures to parts that require deeper understanding of the course (Part (d)). The first part (a) was answered well with a range of examples given. Part (b) of the question was answered very well especially as this was an in-depth mechanism. Part (c) of the question proved a bit more challenging with the first two parts answered well and the third part which

went through a cationic mechanism not a radical mechanism was not answered to the same standard. The final part of the question (d) was answered either very well or proved difficult. The marks given for this question was 20% and over half got over 15% where as the other half got below 5%. The major difficulty with this question seemed to be the writing of the radical mechanism. Of the 14 people who took the questions (with the exception of one person) all parts of the question were answered suggesting that there was sufficient time in the 45 mins allocated.

Q35:

This question wasn't very popular, but the majority of candidates who tackled it produced excellent answers. There was good recall of the rutile structure and some excellent discussions of the magnetic coupling within metal oxides. Most candidates could see that ordering in the pyrochlore materials was inhibited by magnetic frustration. Discussion of the Bonner-Fisher approach to modelling the susceptibility of chains were also good, as were descriptions of the temperature variation of the susceptibility in such compounds.

Q36: Some candidates failed to see that it was a good idea to determine the unit cell of the lattice before trying to work out the degree of frustration. Others saw this was the simplest approach, but then forgot to include all the interactions that link the 7-membered hexagonal plaquette to its neighbours. Most candidates did a good job of interpreting the data in part (c), realising that the two values of the Curie constant they could derive were incompatible and that one gave an unrealistically high  $g$  value. There were some very sophisticated applications of Mean Field Theory to take account of different numbers of nearest neighbours in the lattice. Most candidates were able to get at least part of the way to a sensible magnetic structure in part (e), some invoked spin canting, for which the measured magnetisation is much too large.

Q 37

Generally answered well. (A) most students got the right idea but answers varied in their level of detail of explanation. (B) contained some errors in the transition state and other manipulations. (C) was generally well explained for the first part and many got that complexing cobalt to the alkyne would be effective. Few got the Lewis acid on the pyridine but several proposed making the N-oxide, which was also given credit. (D) A variety of answers, as might be expected for an open question such as this, all reasonable ones given credit. Average Mark – 16.6

Q 38

Overall, the questions was generally well answered with varying degrees of detail and care in the answers and mechanisms. (A) most got the basic mechanism but few saw the exo double bond will likely isomerise with Pd(II) via reinsertion. (B) well attempted. (C) some had difficulty following the course of the cascade cyclisation. (D) most rationalised the zirconium chemistry reasonably well and the alkyne insertion that followed. Average Mark – 16.9

Q40 - 30 scripts

Average mark 17.1/25

On the whole, the fundamental pyrrole reactivity and ring construction part was understood well, with many of the candidates scoring highly in these sections. A wide variety of answers came from the final part: most identified the alcohol condensation and made good attempts at mechanisms. The cation rearrangement was only given a plausible

mechanism by a smaller cohort with many cyclisations and fragmentations leading nowhere. Some credit was given to those that explicitly identified that the formyl group must have migrated to the 3-position from the 2.

#### Q42

This question was attempted by 36 candidates and was generally well answered.

Part a was reasonably attempted, although a surprisingly large number of candidates could not give the correct structure of SDS and a few could not recall C16TAB. The Wilhelmy plate method followed by capillary rise and then drop shape were the preferred methods given for surface tension determination. Most candidates made a reasonable attempt and included the appropriate equation used to extract the required parameter. Other than a few minor slips, generally well done. Part c and d were well answered with only one or two exceptions. Part e had a number of sections, but most candidates managed to make a good attempt. A few errors included plotting the wrong axes (despite being told what to plot), taking the gradient at the wrong point of the data and rather poor comments about the determined area per molecules (larger than normal due to charge repulsion). However, the changes on adding salt (reduced area) and the origin of the change in gradient (CMC) were generally well answered. The addition of alcohol that stabilises the ionic surfactants in the micelle (and hence lowers the CMC) was identified in many cases. The last part of the question caused most difficulties, but even then the reduction of the surface tension was identified by a good fraction of candidates and one candidate correctly identified that the impurity would go into the micelle at the concentrations greater than the CMC.

#### Q43

Almost all students correctly determined the number of electron pairs for cluster bonding in  $B_8Cl_8$ . Many noticed that the cluster was electron deficient but not all spotted that it is hyper electron deficient. Half a mark was awarded for the former and a full mark for the latter observation.

- (a) Students who spotted that the cluster involved  $B_3$  bridges, similar to those observed in  $B_4Cl_4$  were awarded a further mark. This normally involved spotting that these bridges were 3c, 2e bonds (1 mark) and that the faces of the polyhedron would most likely be triangular. This aspect of the bonding – deltahedra consist of triangular faces – is important since it is this arrangement that results in the most delocalised structures with bonding of this nature. Any cluster shape involving only triangular faces was awarded a mark. Half marks were awarded for suggestion that the structure was a cube (square faces) made up of  $B_4$  bridges.

Mistakes were made by those who tried to use Wade's Rules to examine the bonding of this cluster. Wade's Rules are not appropriate in this case since the cluster is too electron deficient.

#### Q43:

This question was answered quite well, albeit by only a small number of candidates, with marks ranging from 13 to 18, and an average mark of 16.3 (over 6 scripts). Part (a) was somewhat challenging, involving the application of ideas from the notes (and supervision questions) to an unfamiliar situation. Only one candidate produced a near-perfect answer, but most of the others gained a few marks by showing that they knew how to approach the problem, even if they slipped up (or gave up) on their way to the final answer. Part (b), involving the interpretation of XPS data,

was answered entirely correctly by all candidates, but Part (c) on the interpretation of NEXAFS data was more of a mixed bag (in some cases, candidates failed to eliminate possibilities that were contradicted by the data in the preceding part of the question). Parts (d) and (e), on the other hand, were uniformly very well answered, albeit they were much closer to the notes in terms of the required discussion. Overall, whilst the number of candidates attempting this question was disappointing (presumably many were put off by the unfamiliarity of the first part) those who did so found sufficient opportunity to obtain decent marks.

#### Q44

This question was tackled very well by most candidates, with marks ranging from 10 to 25, and an average of 17.8 (over 12 scripts). Part (a) was essentially covered in the notes, and all but a few candidates clearly recalled the derivation with relative ease. Part (b) required some elaboration on topics mentioned in the notes, but again most candidates obtained full marks here too. Part (c) was notable for a surprising spread in marks, even though the topic was again essentially based on the notes; a number of candidates drew inaccurate orbital energy diagrams, leading to erroneous discussion of the implications for stability. Part (d), on the Stoner model in cases of covalent adsorption, was answered well by almost all candidates. On the other hand, Part (e), which required candidates to go beyond the notes in suggesting what might happen upon ionic adsorption, gave rise to more varied answers; whilst only a few candidates gave more-or-less complete discussions, however, most did have some good ideas here. The overall performance on this question was gratifying, albeit the question was relatively pedestrian compared with the preceding one.

#### Q45

This question was extremely well answered by the three candidates who attempted it, each demonstrating a good understanding of the basics of quantum scattering theory and partial-wave analysis. The places where candidates did lose marks were in a(iv) (where one candidate failed to notice that the orthogonality relations for Legendre Polynomials are given in the data book), and in b(i), where only one candidate was able to account fully for the behaviour of the phase shift on passing through the resonance energy.

#### Q46

Only two answers and both of the essentially perfect. This course only attracts very few students but evidently the bright ones. Also this years question was perhaps a bit on the easy side with ample preparation in the examples. Still I am happy that these two students understood what this course was about and they fully deserve the high mark they got.

Q47: Fewer than I would have anticipated explained the ionization of product 1 in different solvents well enough to get full marks; many obtained partial credit. More explained the mode of binding of 1 to the porphyrin, and responses were generally good as to the flexibility of 2 enabling the binding of guests having different lengths. Many got the Rh binding right in part e, although some invoked displacement of the acac (bidentate) ligand as opposed to the CO (monodentate) ligand, for partial credit.

Pleasingly many picked up the clue about Rh-P dipolar coupling in the NMR in order to verify their answer.

Q48: Quite a few attempted this stereochemistry-centric question, with generally good results. Most understood that statistical factors lead to the 3:1 mer:fac ratio in 48a, although quite a few questionable structures for the TREN adduct were postulated in 48b. Most understood the entropic driving force for substitution in 48c, and many reasonable answers were credited to explain the stereoselectivity observed in 48d (mostly variations on a quadrupole-quadrupole theme, correctly). The vast majority got 48e right, including the stereochemistry, whereas a majority noted (incorrectly) that product 4 should be a cube, for partial credit only. Very few got 48g right, noting the conversion of the tetragonal prism into a tetrahedron, although many predictions were explained well, obtaining substantial partial credit.

Q49: Some excellent answers especially with regard to the electron microscopy and PXRD comparison. It required a good critical comparison and this was on the whole done well. Part (c) was based on a topic briefly mentioned in the lectures and supervisions and again it was good to see that candidates were able to clearly summarise the key issues. Part (d) was, however, very disappointing. Although the phenomenon had been presented in the lectures, and a suitable crystal analysis given, few really explained well the failure to obtain the succinic acid cocrystal.

Average mark: 17.92. 13 attempts

Q50: Generally a good level of preparation was noted although in Part (a) none of the students gave a completely satisfactory answer. For example, most of them correctly proposed a mixture of solvents as a tool for avoiding solubility problems, although none mentioned that this often can imply a modification of the crystallization technique from evaporation to cooling crystallization. In Part (b) most students proposed valid alternatives, although some errors could be also noticed such as classifying freeze drying as a mechanochemical technique. Part (c) was based on a topic that required additional reading and I was happy to see that most candidates were able to answer this well. Part (d) required a good knowledge about the mechanistic aspects of mechanochemical cocrystal formation and this was also on the whole answered properly.

Average mark: 17.38 (8 attempts).

Q. 53

Only answered by 6 candidates, two of which did not finish the question, which explains the rather low average of 13.6 out of 25. Of the 4 who finished the question two were good, one average and one poor. Good answers used AHBA as the starter unit for the PKS and did as many common steps as possible before the pathways to Divergolides A, B, and L diverged.

Q. 54

Answered by 8 candidates, two of which did not finish the question. Most of those that did finish did well. Part (a) was generally well answered with just a couple of the more subtle points being missed by all. In part (b) most recognised that PR toxin is a terpene but some thought it was a polyketide - these latter could get ca. 60% of the marks for a workable scheme along these lines. Average mark 16.75 out of 25.

IDP Q1

Generally answered well, the candidates showing good knowledge of atmospheric chemistry and circulation processes. Some candidates failed to calculate the photolysis rate correctly,

either using the wrong cross section or failing to recognise how to use the ozone column density.

22 answers, mean mark 16.9

#### IDP Q2

Most candidates knew how to calculate the surface and atmospheric temperatures, using the information given. Some failed to remember that an emissivity factor needed to be included in calculating the atmospheric temperature. The most challenging part of the question called for a quantitative estimate of the change in stratospheric temperature. There were a small number of pleasing, first class attempts which recognised that the stratospheric contribution needed to be weighted by its pressure.

23 answers, mean mark of 17.0

#### IDP Q3

This was a fairly (too?) straight forward question. Most attempts managed the quantitative sections successfully.

19 answers, mean mark of 17.1