

# Structure of the Layered Intercalate $\text{TaS}_2\{\text{Co}(\text{Cp})_2\}_{0.25}$ : A Powder X-ray, Neutron Diffraction, and Solid-State NMR Study

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In this paper the results of a structural investigation into the superconducting intercalate  $\text{TaS}_2\{\text{Co}(\eta\text{-C}_5\text{H}_5)_2\}_{0.25}$  are described. X-ray diffraction studies have revealed that the host layers are highly ordered in this compound and that intercalation is accompanied by a shift of adjacent  $\text{TaS}_2$  layers by  $\sqrt{1/3} a$  along the  $[\bar{1}10]$  direction relative to their position in the pristine host lattice. Such a shift is driven by specific guest–host interactions. The X-ray structure has been refined by Rietveld profile analysis to  $R_F = 6.7\%$ ;  $P3$ ,  $a = 3.330(1)$ ,  $c = 23.040(8)$  Å. Variable-temperature neutron diffraction studies have been performed on  $\text{TaS}_2\{\text{Co}(\eta\text{-C}_5\text{D}_5)_2\}_{0.25}$  to investigate the guest molecules orientational preferences and dynamical properties. These neutron diffraction data suggest that the guest molecules adopt an ordered superlattice and a single orientation with their principal molecular axis parallel to the host layers at all temperatures. Above approximately 280 K the molecules can undergo reorientation around the normal to the layers, but, on cooling, this motion is gradually frozen out, leading to the growth of additional reflections in the diffraction pattern.

## Introduction

Since the discovery of the superconducting amine intercalates of  $\text{TaS}_2$  and other layered chalcogenide lattices some 20 years ago, there has been considerable interest in the physical properties of these layered materials.<sup>1–7</sup> Indeed the desire to study the effects of the inclusion of guest molecules, and in particular paramagnetic species, between the superconducting layers led Dines to the discovery of the metallocene intercalates of the layered metal sulfides.<sup>8,9</sup> Since that time there have been a large number of such compounds prepared, and many investigations into their physical properties.<sup>10–14</sup>

Until recently the detailed structure of these metallocene intercalates has remained largely unknown; there have been no complete structural refinements

published. In addition, there has been some debate in the literature as to the orientation and motional properties of the guest molecules. In the case of the cobaltocene intercalate of  $\text{TaS}_2$  there have been two main studies on the dynamics of the guest molecules, which have suggested different conclusions concerning the guest orientation.

In the first study, Silbernagel employed solid state proton NMR to probe the properties of the guest molecules. He reported that the line shape of the cyclopentadienyl proton resonance in  $\text{TaS}_2\{\text{Co}(\eta\text{-C}_5\text{H}_5)_2\}_{0.25}$  underwent two distinct broadenings on cooling; an initial broadening from approximately 245 K, followed by a second broadening from approximately 80 K.<sup>15</sup> Quantitative analysis of these results suggested that the most likely model was one in which the guest molecules adopt an orientation with their principal ( $C_5$ ) molecular axis parallel to the plane of the host layers (Figure 1) and that at high temperature the molecules can spin about an axis perpendicular to these layers (and therefore parallel to the host  $c$  axis). On cooling, however, this second motion becomes frozen out, giving the observed 245 K broadening.

In a more recent study, Heyes et al. have monitored the temperature dependence of the solid state  $^2\text{H}$  NMR line shape of  $\text{TaS}_2\{\text{Co}(\eta\text{-C}_5\text{D}_5)_2\}_{0.25}$ .<sup>16,17</sup> At low temperature, a single Pake doublet was observed. On warming to approximately 230 K, the growth of an inner Pake doublet, shifted slightly upfield relative to the outer doublet, and of approximately half its splitting was observed. From these data a model was suggested whereby at low temperature solely the *perpendicular* guest orientation is present between the layers, but as

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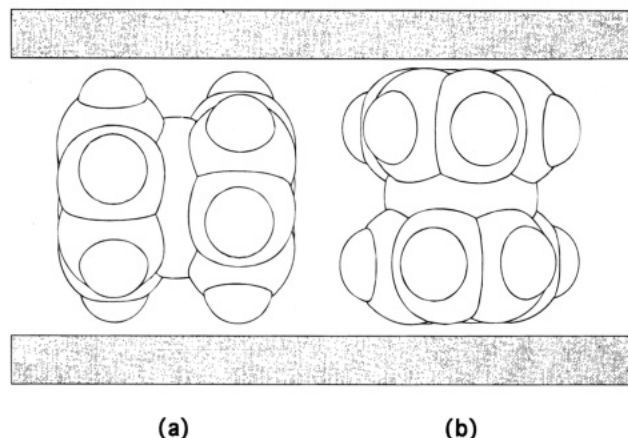
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**Figure 1.** The two low-energy orientations postulated for metallocene molecules between the layers of a metal dichalcogenide, with the principal molecular axis either (a) parallel or (b) perpendicular to the host lattice layers.

the sample is warmed the guest molecules undergo a reorientation until at room temperature some 30–50% of the molecules adopt the *parallel* orientation.

Over the past few years we have investigated the orientational preferences of a number of simple unsubstituted metallocene molecules by a combination of X-ray and neutron diffraction techniques on both powders and single crystals and by solid-state  $^2\text{H}$  NMR. In all cases it seems that the guest molecules adopt the parallel orientation between the layers.<sup>13,18–22</sup> Further support for the parallel orientation comes from IR studies on the closely related metal phosphorous sulfides.<sup>23,24</sup> The only other evidence for the perpendicular orientation and the reorientation of guest species over a period of time has been obtained by in situ diffraction experiments on the substituted metallocene  $\text{Mo}(\eta\text{-C}_6\text{H}_3(\text{CH}_3)_3)_2$  intercalate of  $\text{ZrS}_2$ .<sup>25</sup> In light of these conflicting reports it was decided to reinvestigate the properties of the title material.

### Experimental Details

**TaS<sub>2</sub>.** 2H TaS<sub>2</sub> was synthesized using a combination of the methods of Revelli and Heyes,<sup>17,26</sup> although, to attain the desired polytypic purity, a modified cooling procedure was adopted. TaCl<sub>5</sub> (25.0 g, Aldrich, 99.9%) was purified by vacuum sublimation at  $10^{-2}$  Torr and 140 °C. 12.0 g was loaded into an alumina boat and warmed to 200 °C over 90 min under a constant stream of H<sub>2</sub>S. The furnace was maintained at 200 °C for 2 h and then warmed to 900 °C for a further 3 h. The resulting black powder was heated to 200 °C under vacuum to remove any volatile impurities, then sieved to <90 μm under an inert atmosphere, and annealed at 900 °C for 24 h in an evacuated quartz ampule. This procedure gave the 1T polytype. The 2H polytype was formed from the 1T polytype by slow cooling from 900 °C to room

temperature over 20 days. The polytypic purity was confirmed by X-ray diffraction and gave good agreement with published data. Cell dimensions of the pure 2H phase obtained were  $a = b = 3.315(2)$ ,  $c = 12.058(9)$  Å, and  $\gamma = 120^\circ$ .

**Cobaltocene.**  $\text{Co}(\eta\text{-C}_5\text{H}_5)_2$  was synthesized according to literature methods.<sup>27</sup> Perdeuteriocobaltocene,  $\text{Co}(\eta\text{-C}_5\text{D}_5)_2$  was synthesized by the reaction of  $\text{Co}(\text{acac})_2$  with  $\text{Na}(\text{C}_5\text{D}_5)$ . Sodium metal (30.0 g) was added gradually to 250 cm<sup>3</sup> of deuterium oxide at 2 °C, yielding ca. 250 cm<sup>3</sup> of approximately 20% W/V NaOD in D<sub>2</sub>O. This solution (50 cm<sup>3</sup>) was added to 50 cm<sup>3</sup> of DMSO and 50 cm<sup>3</sup> of cyclopentadiene monomer. The mixture was stirred for 1 h, the cyclopentadiene monomer (top layer) decanted off, and the procedure repeated a further four times. The crude monomer was then distilled (40 °C) to give the pure deuterated monomer; yield = 35.0 cm<sup>3</sup>, 70%. The extent of deuteration was estimated to be >95% by mass spectroscopy.  $\text{Na}(\text{C}_5\text{D}_5)$  was prepared by the dropwise addition of the deuterated monomer to finely divided sodium metal in THF, followed by 3 h of stirring at room temperature. The resulting mixture was filtered, and the solvent removed under reduced pressure yielding a white powder. All manipulations of cyclopentadienyl compounds were performed under a nitrogen atmosphere.

**Intercalation.** Intercalation was achieved by stirring a suspension of the host lattice in a toluene solution containing a 4-fold molar excess of the guest molecule at 120 °C for 4 days. Samples were washed with  $5 \times 10$  mL of dry toluene, and their stoichiometry was determined by elemental analysis.  $\text{TaS}_2\{\text{Co}(\text{C}_5\text{H}_5)_2\}_{0.25}$  observed (calculated) composition: C 10.1 (9.0) %; H 0.85 (0.85) %; Co 5.3 (5.0) %.

**Measurements.** Powder X-ray patterns were recorded with Cu K $\alpha_1$  radiation produced by a Ge(111) monochromator in transmission geometry on samples sealed in 0.2 mm capillaries using a Siemens D5000 diffractometer equipped with a linear position sensitive detector. Due to the highly absorbing nature of the sample and high background due to cobalt fluorescence, a step size of 0.05° and total scan time of 72 h were used. In situ X-ray diffraction patterns were recorded at the U. K. Synchrotron Radiation Source (S.R.S.) using an experimental setup that has been described in detail elsewhere.<sup>28–30</sup> Neutron diffraction patterns were recorded on the Polaris spectrometer at the ISIS pulsed neutron source of the Rutherford Appleton Laboratory, UK. Solid-State  $^2\text{H}$  NMR spectra were recorded on samples sealed under nitrogen in Pyrex tubes at 30.7 MHz using a Bruker MSL 200 spectrometer. The quadrupole spin-echo technique<sup>31</sup> with standard precautions and phase cycling was used to acquire the spectra.<sup>32–34</sup> Further details of the spectrometer set up have been described elsewhere.<sup>35</sup> A spin echo delay of 20 μs and recycle delay of 10 s were used.

### X-ray Diffraction Studies

The powder X-ray diffraction pattern of  $\text{TaS}_2\{\text{Co}(\text{C}_5\text{H}_5)_2\}_{0.25}$  is shown in Figure 2. The pattern contains a number of sharp reflections, indicating that this intercalate has a significant degree of 3 dimensional order. In particular, none of the broad (*hkl*) reflections often observed for pristine 2H-TaS<sub>2</sub> is present, suggest-

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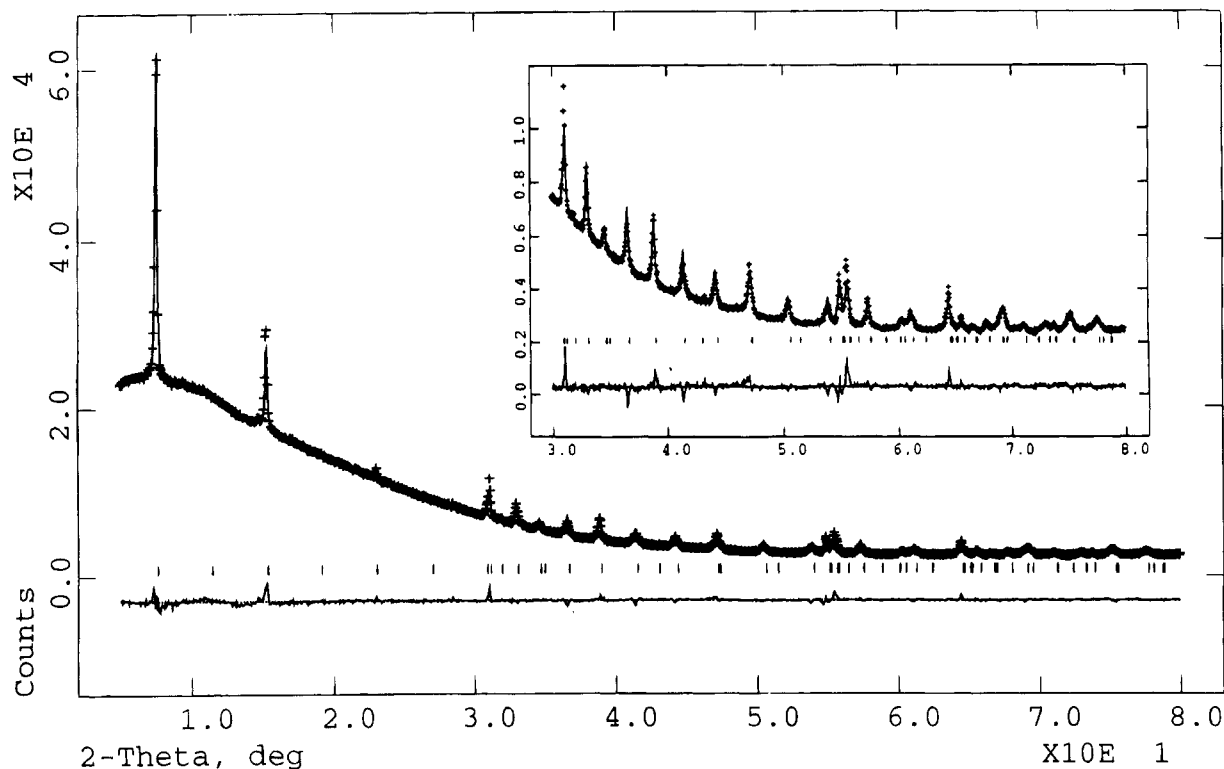
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**Figure 2.** Rietveld refinement of  $\text{TaS}_2\{\text{Co}(\text{Cp})_2\}_{0.25}$ . Observed (+), calculated (full line), and difference plots are shown. Insert shows expansion of the high-angle region.

ing that the intercalate has better interlayer order than the host material. [Additional support for such an increase in layer stacking order on intercalation comes from the observation that the intercalation of a mixed polytype host material (containing (001) reflections at a range of  $d$  spacings prior to intercalation) gives rise to an identical single product phase.] All the observed reflections could be indexed on a cell with similar  $a$  and  $b$  dimensions to the pristine host, and a  $c$ -axis of 23.04 Å ( $a = b = 3.330(1)$ ,  $c = 23.040(8)$  Å,  $\gamma = 120^\circ$ ). Such a  $c$  axis suggests a model containing two layers in the repeat unit and in which an increase in interlamellar spacing of  $(23.04 - 12.06)/2 = 5.49$  Å has occurred on intercalation. Such an expansion is typical for simple unsubstituted metallocenes.<sup>13</sup>

Integrated intensities of the reflections of Figure 2 were extracted by the Le Bail method within the GSAS package<sup>36</sup> and used to calculate a Patterson map in space group  $P3m1$ . Assignment of the strongest peak, at  $(2/3, 1/3, 1/2)$ , to the interlayer Ta-Ta vector suggested that intercalation gives rise not only to an expansion of the layers along the  $c$  axis but also to a shift of adjacent layers in the  $ab$  plane such that Ta atoms no longer lie directly above and below each other as in the pristine host lattice. Introduction of Ta atoms at  $(0, 0, 1/4)$  and  $(2/3, 1/3, 3/4)$ , followed by least-squares refinement and difference Fourier synthesis, revealed S atoms at  $(1/3, 2/3, z)$  ( $z = 0.25 \pm 0.065$ ,  $0.75 \pm 0.065$ ), indicating that the trigonal prismatic Ta coordination is retained on intercalation. Introduction of S atoms at these sites followed by further cycles of least squares refinement and difference synthesis revealed significant interlamellar electron density due to the guest molecules and indicated likely Co sites as  $(1/3, 2/3, 0.0)$  and  $(1/3, 2/3, 0.5)$ .

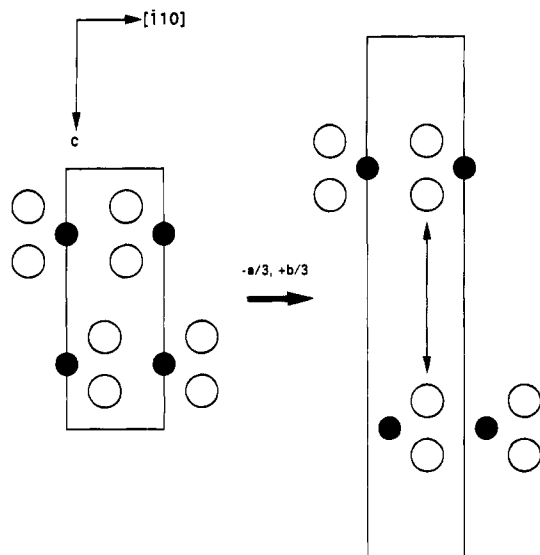
**Table 1. Details of Refinement of  $\text{TaS}_2\{\text{Co}(\eta\text{-C}_5\text{H}_5)_2\}_{0.25}$  in  $P3$**

$a$ (Å)	3.330(1)
$c$ (Å)	23.040(8)
zero point (degrees $2\theta$ )	-0.0012(1)
absorption, $A_h$	2.3
Ta $U_{\text{iso}}$ (Å <sup>2</sup> )	0.027(2)
S $U_{\text{iso}}$ (Å <sup>2</sup> )	0.038(5)
Co, C $U_{\text{iso}}$ (Å <sup>2</sup> )	0.12(3)
preferred orientation, $R_o$	0.837(6)
$S_z$	0.25, $0.75 \pm 0.0651(6)$
$\chi^2$	4.23
$R_{\text{WP}}$	2.31%
$R_{\text{P}}$	1.48%
$R_{\text{F}}$	6.7% (91 reflections)

<sup>a</sup> S  $z$  coordinates restrained to symmetrical heights above and below the Ta layer. A pseudo-Voigt peak shape function and a shifted Chebyshev background function with 12 terms were used. 5–80° data were used in refinement, giving 1500 profile points. A total of 25 parameters were refined in final cycles. Observed and calculated structure factors are available as supplementary data.

Refinement of this model gave reasonable agreement between observed and calculated profiles ( $\chi^2 = 7.3$ ,  $R_{\text{F}} = 9.15\%$ ). For the final stages of refinement space group  $P3$  was adopted, and scattering from the rotating (vide infra) guest molecules was modelled by the introduction of a cobaltocene molecule in the parallel orientation with the Co atom on the 3-fold site determined above. Such a 3-fold disordered guest molecule was found to provide a reasonable model of the rotating guest. Least-squares refinement gave good agreement between observed and calculated profiles (Figure 2) and a final agreement factor,  $R_{\text{F}}$ , of 6.75%. Details of the refinement are given in Table 1. Attempts were also made to model the reorientation of the cyclopentadienyl rings around the metal-ring centroid by introduction of disorder in the ring carbon positions. No improvement in the fit was obtained.

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**Figure 3.** Schematic representation of how a shift of adjacent layers by  $(-a/3, +b/3)$ , i.e., a shift of  $\sqrt{1/3}a$  along the  $[\bar{1}10]$  direction gives rise to a structure in which S atoms of adjacent layers lie directly above and below one another. Such a shift destroys the interlamellar octahedral and tetrahedral holes occupied by small ionic guests, giving solely trigonal prismatic interlamellar sites.

### Discussion of the X-ray Structure

X-ray diffraction is a powerful method for locating the heavy atoms of the host layers since some 81% of  $F_{000}$  is due to the Ta and S atoms. This dominance of the scatter by the host layer means, however, that relatively little information about the guest molecules can be obtained; discussion of their packing is therefore postponed until later. Intercalation gives rise to a shift of adjacent layers by  $(-a/3, b/3)$ , or a shift of  $\sqrt{1/3}a$  along the  $[110]$  direction (Figure 3), such that S atoms in adjacent layers lie directly above and below each other, giving rise to "chains" of S atoms parallel to the  $c$  axis. Such a structure retains the  $P63/mmc$  symmetry of the pristine host lattice, though, for reasons described below, structural refinement was carried out initially in  $P3m1$ , and finally in  $P3$ .

The driving force for such a regular layer shift appears to be the formation of a favorable coordination site for the ionized guest molecules. The preference of the guest molecule for a lattice site in which the Co atom of the (rotating) guest molecule lies directly above and below an S atom of the layers appears to force the stacking sequence observed and gives rise to a structure with a high degree of 3-dimensional order. Evidence of similar layer shifts has been obtained for the ferrocene intercalates of the layered lattice  $FeOCl$ ,<sup>37,38</sup> and also for the ammonia intercalates of the layered metal chalcogenides.<sup>39-42</sup>

While the observed and calculated profiles of Figure 2 show that such a layer shift provides a good structural

model, the final  $R$  factor ( $R_F = 6.7\%$ ) is perhaps not as low as might be expected. The principal factor determining the layer stacking sequence has been described as the attainment of a favorable guest coordination by sulfur. Consideration of the structure of pristine host layers reveals that in addition to the proposed "layer shift" such a S arrangement can also be achieved by the rotation of alternate layers by  $60^\circ$  around the  $c$  axis from their position in the pristine host, leading to a layer structure of symmetry  $P6m2$ . Two-phase refinement in space group  $P3m1$  (a subgroup of both  $P63/mmc$  and  $P6m2$ ) suggested that the proportion of the rotated model was less than 5(2)%. Such a dominance of the layer shift model is sensible on energetic grounds, since it requires minimal disturbance of the layers on intercalation. While the two displacements seem superficially of similar magnitude, it must be remembered that a small local rotation at one position in a crystallite requires significant lateral displacement of atoms several unit cells distant from the rotation center.

It is, however, likely that under the relatively harsh intercalation conditions (toluene at  $120^\circ C$ ), a significant proportion of stacking faults of the "rotation" type will be present in the material. Such faults which leave the  $z$  coordinates of the atoms unchanged, will not affect the intensity of the  $(00l)$  reflections, but will alter the intensity of general  $(hkl)$  reflections. Indeed examination of the difference curve of Figure 2 reveals that the principal residual peaks are all  $(00l)$  reflections (those at  $31.01$ ,  $55.79$ , and  $64.65^\circ 2\theta$  being the  $(008)$ ,  $(0014)$ , and  $(0016)$  reflections, suggesting that such stacking faults are responsible for the relatively high final  $R$  factor.

The occurrence of the layer shift is perhaps best shown by the data of Figure 4, which shows the evolution of the diffraction pattern of the host-guest combination as a function of time. Spectra were recorded on a stirred suspension of the host material in a toluene solution of cobaltocene at the UK Synchrotron Radiation Source (S.R.S.) using an experimental setup described elsewhere.<sup>28</sup> Figure 4a shows a 0-80 keV range with a detector angle of  $1.89^\circ$ . In energy-dispersive mode the familiar Bragg equation becomes  $E(\text{keV}) = 6.19926/d \sin \theta$ . The disappearance of the host  $(002)$  reflection at  $62.2$  keV ( $6.05 \text{ \AA}$ ) and the appearance of the intercalate  $(002)$  and  $(004)$  reflections at  $32.5$  keV ( $11.58 \text{ \AA}$ ) and  $65.0$  keV ( $5.79 \text{ \AA}$ ) are clearly visible. It can be seen that the reaction proceeds via a direct reactant to product route, and no more complex phenomena such as staging are observed.

Figure 4b shows a 30-60 keV range at a detector angle of  $5.81^\circ$ . The  $(100)$  and  $(102)$  peaks of the pristine host are clearly visible at  $t = 0$ . As the reaction proceeds new  $(10l)$  peaks are seen growing into the pattern. The observation of strong  $(10l)$   $l \neq 2n$  reflections is characteristic of a shift of adjacent layers. Due to the pressures on beam time, the reaction of Figure 4b was not run to completion; inspection of the low-angle regions of this sample suggested that the reaction was approximately 60% complete at  $t = 6$  h.

### Guest Molecule Behavior

Solid-state  $^2H$  NMR spectra of  $TaS_2\{Co(\eta-C_5D_5)_2\}_{0.25}$ , shown in Figure 5, are very similar to those previously reported.<sup>16,43</sup> The separation of the discontinuities of

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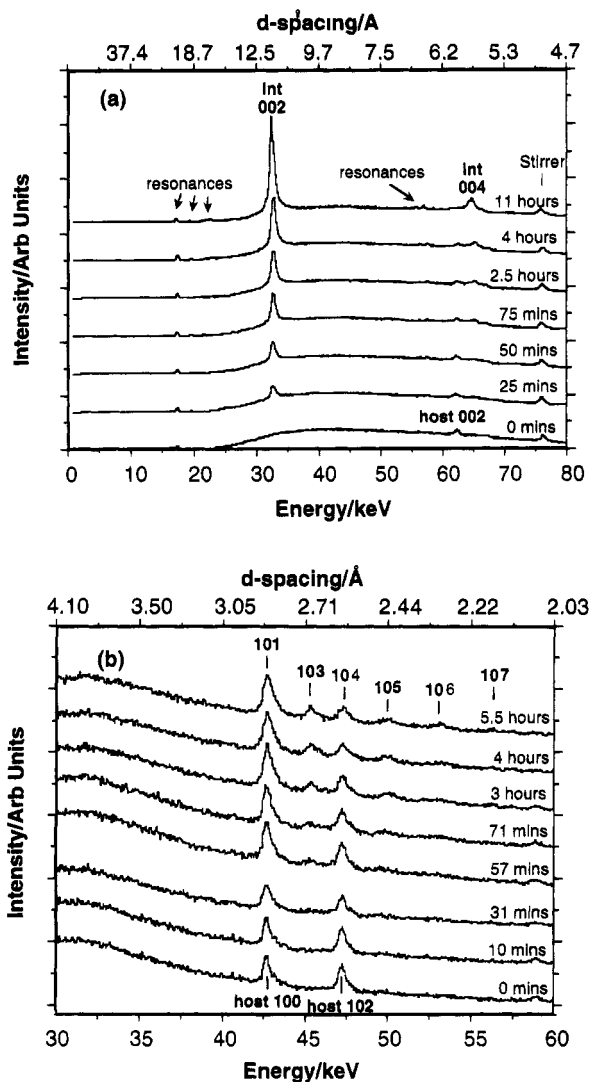
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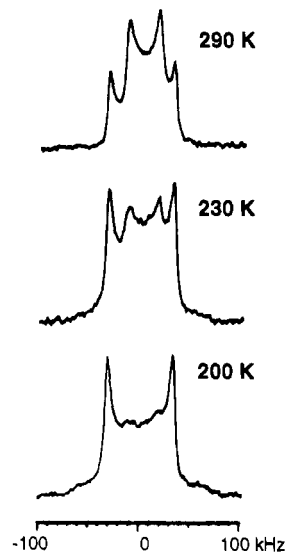
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**Figure 4.** In situ powder diffraction patterns of  $\text{TaS}_2/\text{Co}(\eta\text{-C}_5\text{H}_5)_2$  in toluene at 120 °C showing how the diffraction pattern of the host-guest system evolves in real time. (a) Detector angle of 1.89°. The host (002) reflection at 62.2 keV slowly decreases in intensity, while the intercalate (002) and (004) at 32.5 and 65.0 keV gradually increase in intensity. Peaks at 17.6 and 19.6 keV are the Mo  $K\alpha$  and  $K\beta$  resonances (from slit materials), very weak peaks can be distinguished in individual spectra at 56.3 and 57.5 keV due to Ta  $K\alpha$  and  $K\beta$  resonances. The Ta absorption edge can be seen at 67 keV. The peak at 76 keV is due to the stirrer flea. (b) Detector angle 5.81°, temperature 110 °C; dramatic changes in intensity patterns of the (10*l*) series of reflections due to the layer shift can be seen. (107) and Ta  $K\alpha$  overlap at this detector angle.

65 kHz is typical for a cyclopentadienyl ring undergoing rapid reorientation around the metal-ring centroid axis. The observation of the growth of an inner Pake doublet above 200 K clearly shows the onset of additional molecular motion as the sample is warmed. A series of neutron diffraction experiments was performed to investigate the packing arrangement of guest molecules in this compound and to try and determine unambiguously the motional processes responsible for the changes in NMR line shape.

The room-temperature neutron diffraction pattern of  $\text{TaS}_2\{\text{Co}(\eta\text{-C}_5\text{D}_5)_2\}_{0.25}$  shows a large number of sharp



**Figure 5.** Variable-temperature  $^2\text{H}$  NMR spectra of  $\text{TaS}_2\{\text{Co}(\eta\text{-C}_5\text{D}_5)_2\}_{0.25}$  recorded at 290, 230, and 200 K with a spin-echo delay of 20  $\mu\text{s}$ .

peaks, again suggesting a high degree of order in this compound (Figure 6). There are, however, a number of peaks which are not predicted by the simple cell used to index the X-ray pattern. In particular, a strong peak is observed at  $d = 3.3$  Å, which, while being clearly related to the cell of the host layers (hexagonal,  $a = 3.3$  Å), cannot be indexed on the X-ray cell. Simple calculations based on the guest size and the observed chemical occupancy of 0.25 show that only one in four of the possible guest sites identified by X-ray studies can be occupied at any given time. [In the crystal structure of pristine  $\text{Co}(\text{Cp})_2$ , the molecules are essentially close packed in the  $ab$  plane, with their  $C_5$  axis parallel to this plane; exactly the packing arrangement proposed for the intercalated molecules. An estimate for the "area" occupied by the guest molecule is then 41 Å<sup>2</sup>. The unit cell area of  $\text{TaS}_2$  is 9.4 Å<sup>2</sup>, suggesting a packing density of  $9.4/41 = 0.23$ , or approximately one in four lattice sites.<sup>38,44</sup>] This then suggests the adoption of a superlattice structure to describe the guest packing. Indeed all the peaks in the room-temperature neutron pattern can be indexed on a cell  $a = b = 2a(\text{X-ray})$ ,  $c = c(\text{X-ray})$ . Refinement of such a cell gives dimensions  $a = 6.64(2)$ ,  $c = 22.98(5)$  Å,  $\gamma = 120^\circ$ . The relationship between this cell and that of the pristine host is illustrated schematically in Figure 7.

On the basis of such a large supercell, one might expect considerably more superlattice reflections in the neutron pattern. However, even though guest molecules within an individual layer are well ordered, it is unlikely that there is any registry between subsequent guest layers. This 2D disorder, analogous to that well-known for intercalates of graphite, will lead to only ( $hk0$ ) reflections from the guest supercell being present.<sup>45-47</sup> Thus the first peaks expected will be the (100) and (110) reflections of the hexagonal cell at 5.75 and 3.32 Å, respectively. That at 3.32 Å is observed, along with a

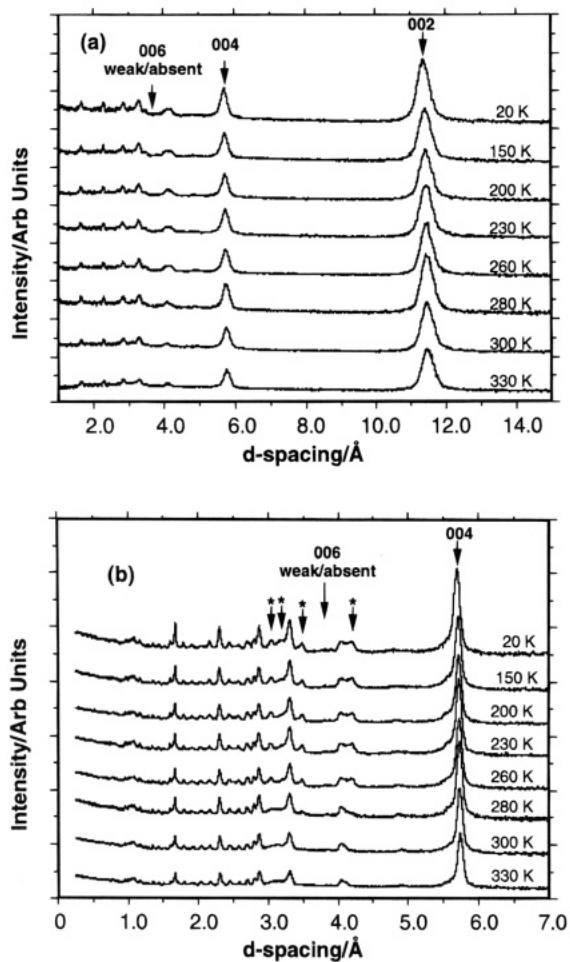
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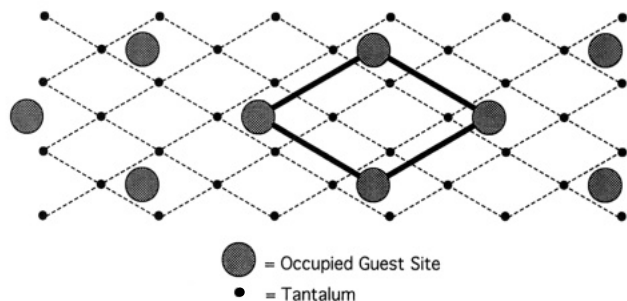
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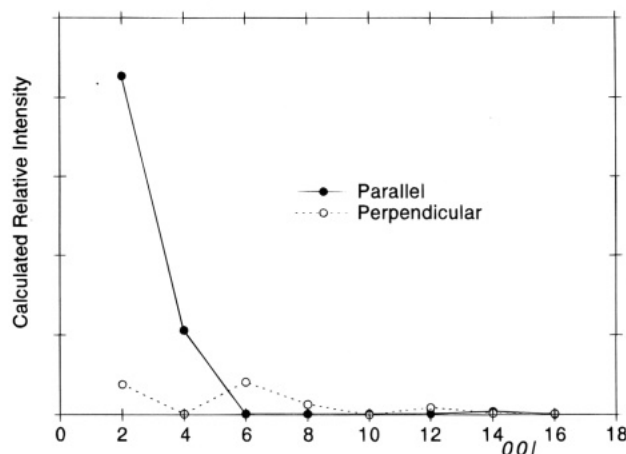


**Figure 6.** Variable-temperature powder neutron diffraction patterns of  $\text{TaS}_2\{\text{Co}(\eta\text{-C}_5\text{D}_5)_2\}_{0.25}$  at a variety of temperatures between 330 and 20 K. (a) Data from Polaris B-bank showing a 0–14 Å  $d$ -spacing range. (b) Data from A bank showing a 0–7 Å  $d$  spacing range. Peaks marked with asterisks appear at low temperature only. The peak at 4.05 Å is an impurity peak and was present in this batch of host prior to intercalation. A second sample containing no such impurity peak showed identical changes in the neutron diffraction pattern as a function of temperature.



**Figure 7.** Adoption of one site in four by the cobaltocene guest molecules leads to a guest supercell of 2a 2b. Host cell shown as dashed line, supercell shown in bold.

broad peak in the diffraction pattern to lower angle. The peak at 5.75 Å, however, lies exactly below the (004) reflection ( $22.98/4 = 5.745$  Å) from which it cannot be distinguished at the experimental resolution. This reflection may, however, be the source of the marked asymmetry of the observed peak, which shows significant intensity to lower  $d$  spacing, reminiscent of the peak shapes observed for other 2D disordered materials.<sup>48–50</sup>



**Figure 8.** Calculated intensities of the (00 $l$ ) reflections for the two extreme orientations of the guest molecule of Figure 1. Intensities were calculated using the program PJWBESS (P. J. Wiseman, Oxford University), which uses a Bessel function to model the scatter from a rapidly rotating cyclopentadienyl ring. Ring temperature factors of  $B = 3.0$  Å<sup>2</sup> were used. For ease of comparison with the time of flight spectra of Figure 6, intensities have been scaled by a  $d^4$  Lorentz correction and a factor to allow for the dependence of peak width on  $d$  spacing.

Investigations on single crystals of other intercalates have shown that the (00 $l$ ) reflections are extremely sensitive to guest orientation and would therefore be expected to show significant changes in intensity if the guest molecules undergo any reorientation between the layers.<sup>18,21</sup> This sensitivity is shown by Figure 8, where it can be seen that the relative intensities of the first three (00 $l$ ) reflections can be expected to change from (strong, strong, weak) to (medium, weak, medium) for any guest reorientation from the parallel to the perpendicular orientation.

It can be seen from Figure 6 that the intensity pattern of the (00 $l$ ) reflections suggests that the guest molecules adopt the parallel orientation, as in the other intercalates studied. Unfortunately the degree of peak overlap precludes the extraction of accurate (00 $l$ ) intensities required for a one-dimensional refinement; in addition the lack of interlayer registry greatly complicates attempts at full-profile analysis. It can, however, be seen that there is relatively little variation in the relative intensities of the (00 $l$ ) reflections over the entire temperature range studied (20–330 K). In particular the (006) reflection, predicted to be strong for the perpendicular orientation, remains extremely weak/absent throughout. This suggests that the guest species retain the parallel orientation throughout and that the motional process observed by <sup>2</sup>H NMR is not the principal molecular axis of the molecules switching from lying parallel to perpendicular to the layer planes. Further evidence for the parallel orientation comes from a recent study on thin films of  $\text{TaS}_2\{\text{Co}(\text{Cp})_2\}_{0.25}$ , where 1D Fourier analysis suggests much better agreement with the parallel than the perpendicular orientation.<sup>51,52</sup>

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Examination of the spectra of Figure 6 does, however, reveal several changes on cooling: (i) significant increases in intensity of, e.g., the  $d = 3.3$  Å peak; (ii) the growth of new peaks at  $d = 3.18$  and  $3.04$  Å from the broad hump in the high-temperature spectrum; (iii) the growth of new peaks at  $d = 3.47$  and  $d = 4.20$  Å.

Identical changes (though at slightly different temperatures) have also been observed on an intercalate prepared from a mixed polytype batch of TaS<sub>2</sub>. These changes were entirely reversible and reproducible in successive cooling/heating cycles. Since they occur at identical temperatures to the line-shape changes in the <sup>2</sup>H NMR, it is reasonable to ascribe them to the same origin.

Although a full structural refinement has proved impractical, it seems reasonable to assume that the extra reflections are a result of the freezing out of molecular motion of the guest molecules in an ordered manner. There is now a considerable body of solid state NMR evidence to suggest that the guest molecules in layered chalcogenide lattices can undergo rotation around the normal to the layer planes. In the case of SnS<sub>2</sub>{Co(Cp)<sub>2</sub>}<sub>0.3</sub> experiments on single-crystal and polycrystalline samples have suggested that molecules with a range of motions about this axis are present at room temperature that as the temperature is raised the distribution of rates of molecular rotation increases.<sup>19</sup> This has now been shown to give rise to powder line shapes very similar to those of Figure 5, albeit without the shift of the central Pake doublet.<sup>14</sup> Thus as the temperature is lowered and the molecules adopt low-energy orientations with respect to each other and the host lattice, extra peaks appear in the neutron pattern. Those at  $d = 3.18$  and  $3.04$  Å, which grow from the region of diffuse scatter to low angle of the (010) reflection, can be tentatively indexed as the (112) and (113) reflections of the hexagonal guest cell.

The origin of the shift of the inner Pake doublet remains unclear. Such a shift indicates a different local electronic or magnetic environment for the two categories of motional molecules (static/spinning). Possible origins of this shift include charge density wave formation, which is known and well documented in pristine 2H TaS<sub>2</sub>,<sup>53,54</sup> or a disorder of the S *z* coordinate. There

has been considerable recent evidence from crystallographic, AFM, and TEM investigations that the S atoms in the S layer can be shifted by up to 0.5 Å from the mean layer plane, which could be the source of the observed chemical shift.<sup>55</sup> Another possibility is that the local susceptibility experienced by the two different types of deuterons is due to a transition from a quasi-continuous motion of the cyclopentadienyl deuterons at high temperature to a more jumplike or "indexed" motion of the Cp rings at lower temperatures.

### Conclusion

The work of this paper has shown that the cobaltocene intercalate of TaS<sub>2</sub> has a high degree of 3-dimensional order. Specific guest-host interactions give rise to a shift of adjacent layers on intercalation resulting in a new stacking sequence. Variable-temperature neutron diffraction studies have shown that the guest molecules adopt a 2a 2b superlattice within the individual layers but that there is little order between subsequent guest layers. On cooling the principal change in the neutron pattern is the growth of several new (*hkl*) reflections, (00*l*) intensities remaining largely unchanged. This suggests that the molecules adopt an orientation with their principal molecular axis parallel to the layers at all temperatures; and consequently that the NMR results suggesting the presence of a mixture of orientations may need reinterpretation. The extra reflections at low temperature arise due to the freezing out of guest rotation around the normal to the host layers; further work will be necessary to explain the precise line shape changes observed in the <sup>2</sup>H solid-state NMR. This work is in progress.

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**Supporting Information Available:** Listing of the observed and calculated structure factors for TaS<sub>2</sub>{Co(Cp)<sub>2</sub>}<sub>0.25</sub> (3 pages). Ordering information is given on any current masthead page.

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