

Structural Characterisation of Organometallic Intercalates of SnSe₂ and ZrS₂ by Neutron and X-Ray Diffraction

Heng-Vee Wong, John S. O. Evans, Stephen Barlow and Dermot O'Hare*

Inorganic Chemistry Laboratory, South Parks Rd, Oxford, UK OX1 3QR

The synthesis of large, single crystals of ZrS₂ intercalated with various organometallic sandwich compounds { [Co(η -C₅H₅)₂], [Cr(η -C₅H₅)₂], [Co(η -C₅H₄Me)₂], [Mo(η -C₆H₆)₂], [W(η -C₇H₇)(η -C₅H₄Me)] and [Ti(η -C₈H₈)(η -C₅H₅)] } and of SnSe₂ intercalated with [Co(η -C₅H₅)₂] are described; results from both neutron and X-ray diffraction experiments reveal that for all the intercalates the organometallic guests reside with their metal-to-ring centroid axes parallel to the layers of the host lattice.

Intercalation into the interlamellar space of metal dichalcogenides modifies the properties of the host material, often quite dramatically; in the case of SnSe₂, intercalation of [Co(η -C₅H₅)₂] converts it from an anisotropic semiconductor to a relatively isotropic Type II superconductor with $T_c = 8.3$ K.¹ While extensive scrutiny has been devoted to studying the physical, magnetic and electrical properties of this class of metal dichalcogenide intercalates,²⁻¹⁰ fundamental questions such as the orientational preferences of the metallocene guests in the interlamellar space still remain largely unresolved and are plagued with conflicting evidence.

Silbernagel's ¹H NMR study in 1975 on TaS₂[Co(η -C₅H₅)₂]_{0.25} concluded that the C₅ axis of [Co(η -C₅H₅)₂] lies parallel to the layers,¹¹ an observation corroborated by Green and coworkers for the ZrS₂ intercalates,¹² where the interlayer lattice expansion was correlated with the sizes of a series of guests, varying from [Cr(η -C₅H₅)₂] to [Cr(η -C₅H₅)(η -C₇H₇)]. However, a detailed deuterium NMR study by Heyes in 1987 suggested that while the [Co(η -C₅H₅)₂] in TaS₂ exists as a

mixture of two orientations¹³ at room temperature, the orientation with the C₅ axis perpendicular to the layers is exclusively adopted at temperatures below 230 K. In contrast, SnS₂[Co(η -C₅D₅)₂]_{0.3} was shown, both by single crystal ²H NMR studies¹⁴ as well as X-ray and neutron diffraction experiments,¹⁵ to consist solely of an orientation of [Co(η -C₅D₅)₂] with the C₅ axis parallel to the layers.

We report here the synthesis of large single crystals (typically 2 × 2 × 0.2 mm) of a series of ZrS₂ and SnSe₂ intercalates, using both symmetrical and unsymmetrical organometallic sandwich complexes, and the application of X-ray and neutron diffraction techniques to study the guest orientation with respect to the layers.

The metal chalcogenide hosts were prepared from the elements. Elemental Zr and S (1 : 2, with a 1% molar excess of S) were heated to 900 °C for 1 week in evacuated, sealed silica quartz ampoules. The purple ZrS₂ with a reddish tinge (ZrS₃) was ground under a nitrogen atmosphere and reannealed at 900 °C for another week to give a free flowing, purple-black

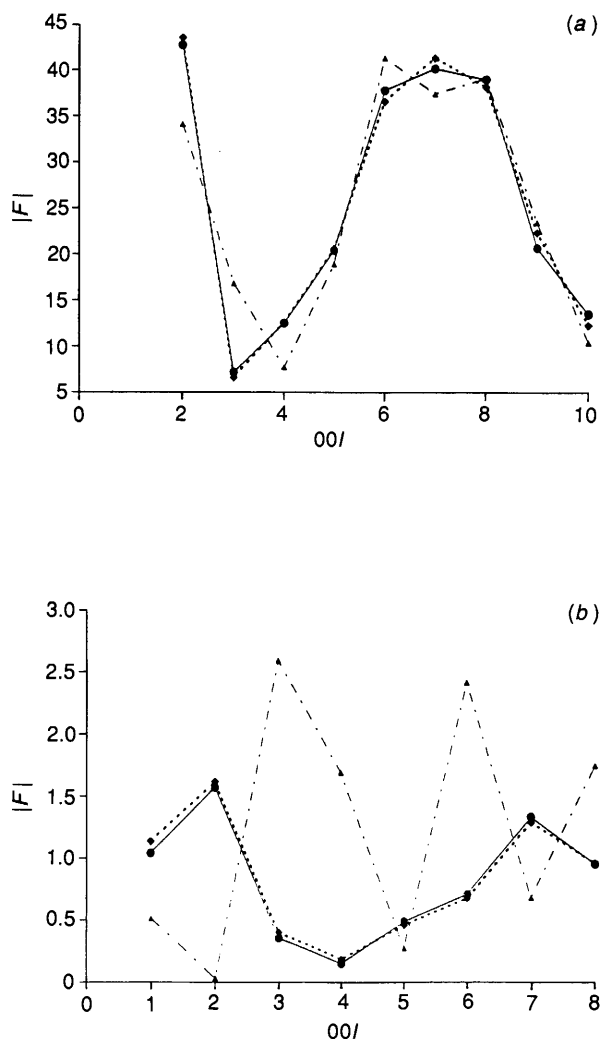


Fig. 1 Comparison of structure factors obtained from $ZrS_2[Cr(\eta-C_5H_5)_2]_{0.20}$ (F_{obs}) vs. structure factors calculated from models in which the $[Cr(\eta-C_5H_5)_2]$ adopts orientations where the C_5 axis lies either exclusively parallel (F_{para}) or perpendicular (F_{perp}) to the host layers: (a) data from neutron diffraction experiments; (b) data from X-ray diffraction experiments. (— F_{obs} , - - - F_{para} , ···· F_{perp})

powder. The purity of the ZrS_2 was checked by powder X-ray diffraction. Small quantities of ZrS_3 impurities, if present, were removed by sublimation at $900^\circ C$ in an evacuated silica ampoule. Large single crystals of ZrS_2 were grown by iodine vapour-phase transport of the ZrS_2 powder, in a linear temperature gradient of 900 to $800^\circ C$. $SnSe_2$ was prepared in a similar manner but at lower reaction and growth temperatures (560 and $510^\circ C$ respectively).

Large single crystals of the intercalate were obtained by heating the crystals (*ca.* $2 \times 2 \times 0.2$ mm) in a sealed Young's ampoule containing a toluene solution of the appropriate organometallic component at $120^\circ C$ for one (ZrS_2 intercalates) or two weeks ($SnSe_2$ intercalates). After intercalation, the plate-like crystals, which had lost their metallic lustre and also expanded visibly along the c -axis, were washed several times with toluene and stored under nitrogen.

X-Ray diffraction patterns of aligned crystals of the intercalates were recorded in Bragg-Brantano geometry so that only $00l$ reflections were collected. Integrated intensities for the $00l$ reflections were extracted after Lorentz, polarization and absorption corrections. Room-temperature neutron diffraction spectra of aligned crystals of both ZrS_2 and $SnSe_2$ intercalates were acquired on the liquid and amorphous diffractometer (LAD) at the Rutherford Appleton Labora-

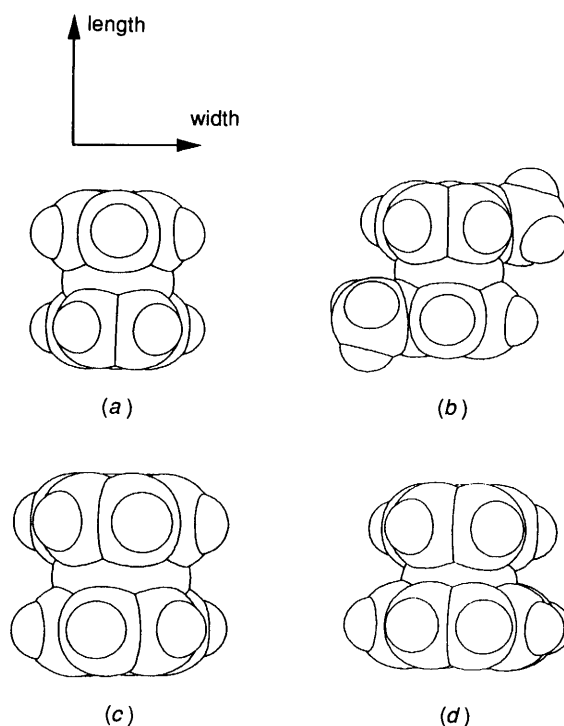


Fig. 2 Space-filling models of various guest molecules showing van der Waals diameters of the constituent atoms: (a) $[Co(\eta-C_5H_5)_2]$; (b) $[Co(\eta-C_5H_4Me)]$; (c) $[Mo(\eta-C_6H_6)_2]$; (d) $[Ti(\eta-C_5H_5)(\eta-C_8H_8)]$

tory, Didcot. The $00l$ intensities derived from both the X-ray and neutron experiments were used to perform subsequent least-squares refinements of the guest orientational parameters.

The c axis dimensions of the intercalates (obtained from least-squares analyses of the X-ray data) are tabulated in Table 1 with the c axis expansion (Δc), stoichiometry and dimensions of the guest molecule. These figures compare favourably with those reported previously.^{9,12,16,17}

Neutron data were only obtained for the symmetrical metallocene guests $[Co(\eta-C_5D_5)_2]$ and $[Cr(\eta-C_5D_5)_2]$ owing to the limited access to neutron beam time and difficulty in obtaining well deuterated samples of the other organometallic guests. However, X-ray diffraction, which is more readily accessible, was used to study a series of intercalates with guests of varying sizes and geometries, ranging from the almost spherically symmetrical $[Co(\eta-C_5H_5)_2]$ to the larger and truncated cone-shaped $[Ti(\eta-C_5H_5)(\eta-C_8H_8)]$ (Fig. 2).

The results of both neutron and X-ray refinements are shown in Table 2. Comparison of the observed and calculated scattering factors, as shown in Fig. 1 for the $[Cr(\eta-C_5H_5)_2]$ intercalate of ZrS_2 , demonstrates the excellent level of agreement between our experimental data and that determined from a model in which all the cobaltocene molecules were oriented parallel to the host layers. The standard deviations on the refined X-ray and neutron data indicate that occupancy refinement tends to be more accurate using neutron data, while the relative S coordinates along the c axis are more precisely determined by using X-ray data refinement. This difference can be rationalized by examining the relative contributions of the guest molecule towards the overall X-ray or neutron diffraction intensity. In neutron diffraction, the guest molecules dominate the overall scattering, making the technique a much more sensitive probe of guest orientation. In contrast, X-rays are predominantly scattered by the host (ZrS_2 or $SnSe_2$) and are therefore a more sensitive indicator of the changes in the S coordinates. However, while X-ray diffraction is a less discriminating probe of guest structure than neutron diffraction, comparison of

Table 1 Comparison of lattice expansion along the *c* axis for SnSe₂ and ZrS₂ intercalates with the dimensions of guest species; length and width conventions are shown in Fig. 2

Compound	<i>c</i> Spacing/ ^a Å	Δ <i>c</i> / ^a Å ^b	Length/ ^c Å	Width/ ^c Å
SnSe ₂ [Co(C ₅ H ₅) ₂] _{0.30}	11.84(1)	5.70	6.96	6.76
ZrS ₂ [Co(C ₅ H ₅) ₂] _{0.25}	11.23(1)	5.41	6.96	6.76
ZrS ₂ [Cr(C ₅ H ₅) ₂] _{0.20}	11.26(1)	5.43	6.96 ^d	6.76 ^d
ZrS ₂ [Co(C ₅ H ₄ Me) ₂] _{0.20}	11.27(1)	5.44	6.96 ^d	7.38
ZrS ₂ [W(C ₇ H ₇)(C ₅ H ₄ Me)] _{0.20}	11.86(3)	6.03	—	—
ZrS ₂ [Mo(C ₆ H ₆) ₂] _{0.20}	11.71(1)	5.88	7.08	7.23
ZrS ₂ [Ti(C ₈ H ₈)(C ₅ H ₅)] _{0.20}	12.20(1)	6.37	6.97	8.15

^a Obtained by least-squares refinement of experimental data. ^b Using *c*(ZrS₂) = 5.83 Å, *c*(SnSe₂) = 6.14 Å. ^c Dimensions of unionised guests (see Fig. 2). ^d Based on [Co(η-C₅H₅)₂] dimensions.

Table 2 Summary of occupancy refinements for both X-ray and neutron diffraction data; the *R*-factor is defined as $[\Sigma(I_{\text{obs}} - I_{\text{calc}})/\Sigma I_{\text{obs}}] \times 100$, where *I*_{obs} and *I*_{calc} are the observed and calculated intensities respectively

Compound (MX ₂ {G})	X-Ray				<i>R</i> -factor (%)	Neutron				<i>R</i> -factor (%)
	S1 coord (z/c)	Parallel ^a occupancy	Perpend. ^a occupancy	% parallel occupancy		S1 coord (z/c)	Parallel ^a occupancy	Perpend. ^a occupancy	% parallel occupancy	
SnSe ₂ [Co(C ₅ H ₅) ₂] _{0.30}	0.134(1)	0.29(2)	0.01(2)	96.7	1.79	0.126(4)	0.291(7)	0.009(7)	97.0	8.15
ZrS ₂ [Co(C ₅ H ₅) ₂] _{0.25}	0.136(1)	0.24(1)	0.01(1)	96.0	1.42	0.126(4)	0.242(5)	0.008(5)	96.8	5.63
ZrS ₂ [Co(C ₅ H ₅) ₂] _{0.20}	0.137(1)	0.18(1)	0.02(1)	90.0	1.28	0.129(4)	0.202(8)	-0.002(8)	100.0	5.05
ZrS ₂ [Co(C ₅ H ₄ Me) ₂] _{0.20}	0.135(1)	0.17(2)	0.03(2)	85.0	3.39					
ZrS ₂ [W(C ₇ H ₇)(C ₅ H ₄ Me)] _{0.20}	0.133(2)	0.16(5)	0.04(5)	80.0	3.51					
ZrS ₂ [Mo(C ₆ H ₆) ₂] _{0.20}	0.122(2)	0.19(2)	0.01(2)	95.0	2.70					
ZrS ₂ [Ti(C ₈ H ₈)(C ₅ H ₅)] _{0.20}	0.122(1)	0.19(1)	0.01(1)	95.0	1.06					

^a Parallel and perpendicular refer to orientations in which the metal-ring centroid axis lies parallel or perpendicular to the layers respectively.

results for [Co(η-C₅H₅)₂] and [Cr(η-C₅H₅)₂] in Table 2 shows it is still a *qualitatively* good indicator of guest orientation. Both methods indicate that the organometallic guests reside with their metal-ring centroid axes parallel to the host layers. This finding is supported by data in Table 1 which show that the *c* axis expansion increases as a function of the width of the guest, while the length remains essentially constant.

Taken together, the data in Tables 1 and 2 allow us to make several observations about the guest orientation and packing between the layers. The ring-to-ring separations of [Co(η-C₅H₅)₂] and [Ti(η-C₅H₅)(η-C₈H₈)] are roughly the same, as is the stoichiometry of their ZrS₂ intercalates. Hence the difference in *c* axis expansion can only be due to a parallel orientation of guest within the host layers. In contrast, [Co(η-C₅H₅)₂] and [Cr(η-C₅H₅)₂] intercalates of ZrS₂ show virtually the same interlayer expansions. Since they have similar molecular dimensions, the difference in stoichiometry of the intercalates reflects the absence of guest close packing in ZrS₂[Cr(η-C₅H₅)₂]_{0.20}. Since [Co(η-C₅H₄Me)₂] is somewhat bigger than [Co(η-C₅H₅)₂] perpendicular to the metal-ring centroid axis, it might be expected to induce a significantly larger *c* axis expansion upon intercalation into ZrS₂. The absence of such a larger expansion suggests that the methyl substituents lie between the sulfur layers, making their effective 'width' the same as [Co(η-C₅H₅)₂].

In conclusion, an array of organometallic guest molecules with varying sizes and geometry have been intercalated into single crystals of ZrS₂. These crystals, along with SnSe₂[Co(η-C₅H₅)₂]_{0.3}, have been examined by X-ray and neutron diffraction in order to extract information as to the nature of the guest orientation between the layers. While the neutron data conclusively demonstrate that both [Co(η-C₅H₅)₂] and [Cr(η-C₅H₅)₂] exist virtually exclusively in an orientation with their principal molecular axes parallel to the layers, we have shown that X-ray diffraction is a more convenient, albeit less discriminating, probe of the guest orientation between the dichalcogenide layers.

We thank A. C. Hannon of the Rutherford Appleton Laboratory for his help in acquiring the neutron diffraction data, D. P.-K. Ng for a kind gift of [W(η-C₅H₄Me)(η-C₇H₇)], the Rhodes Trust for a scholarship to H. V. W., and the SERC for their support.

Received, 9th July 1993; Com. 3/03997H

References

- D. O'Hare, H. V. Wong, S. Hazell and J. W. Hodby, *Adv. Mater.*, 1992, **4**, 658.
- F. J. DiSalvo, *J. Low Temp. Phys.*, 1974, **3**, 417.
- A. H. Thompson, F. R. Gamble and R. F. Koehler, *Phys. Rev. B*, 1972, **5**, 2811.
- W. Biberacher and A. Lurf, *Mol. Cryst. Liq. Cryst.*, 1985, **121**, 149.
- T. H. Geballe, A. Menth, F. J. DiSalvo and F. R. Gamble, *Phys. Rev. Lett.*, 1971, **27**, 314.
- G. R. Miller, *Colloids Surfaces*, 1990, **45**, 243.
- J. M. Vandenberg-Voorhoeve, in *Optical and Electrical Properties*, ed. P. A. Lee, Reidel, Dordrecht, 1976, p. 423.
- D. C. Johnston, *Solid State Commun.*, 1982, **43**, 533.
- C. A. Formstone, M. Kurmoo, E. T. Fitzgerald, P. A. Cox and D. O'Hare, *J. Mater. Chem.*, 1991, **1**, 51.
- D. E. Prober, R. E. Schwall and M. R. Beasley, *Phys. Rev. B*, 1980, **21**, 2717.
- B. G. Silbernagel, *Chem. Phys. Lett.*, 1975, **34**, 298.
- R. P. Clement, W. B. Davies, K. A. Ford and M. L. H. Green, *Inorg. Chem.*, 1978, **17**, 2754.
- S. J. Heyes, N. J. Clayden, C. M. Dobson, M. L. H. Green and P. J. Wiseman, *J. Chem. Soc., Chem. Commun.*, 1987, 1560.
- C. Grey, J. S. O. Evans, D. O'Hare and S. Heyes, *J. Chem. Soc., Chem. Commun.*, 1991, 1380.
- D. O'Hare, J. S. O. Evans, P. J. Wiseman and C. K. Prout, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1156.
- L. Benes, J. Votinsky, P. Lostak, J. Kalousova and J. Klikorka, *Phys. Stat. Sol. (A)*, 1985, **89**, K1.
- J. Votinsky, L. Benes, J. Kalousova, P. Lostak and J. Klikorka, *Chem. Papers*, 1988, **42**, 133.