Organometallic Intercalation of Metal Dichalcogenides: Intercalates of Zirconium Disulphide and Low Ionisation Potential Sandwich Compounds

By Warwick B. Davies, Malcolm L. H. Green,* and Allan J. Jacobson
(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)

Summary The new organometallic intercalation compounds $\{[(\eta^6\text{-}C_6H_6)_2M]_{1/6}ZrS_2\}$ (M = Cr or Mo), $\{[(\eta^6\text{-arene})_2Mo]_xZrS_2\}$, (arene = toluene or mesitylene, $x < \frac{1}{6}$), $\{[(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Cr]_{1/4}ZrS_2\}$, $\{[(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)Cr]_{1/4}ZrS_2\}$, $\{[(\eta^5\text{-}C_5H_5)_2Cr]_{1/4}ZrS_2\}$, and $\{[(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5H_5)Ti]_{1/4}ZrS_2\}$ have been prepared and characterised.

Dines has shown recently that cobaltocene and chromocene react with a number of layered metal dichalcogenides to form intercalation compounds of which $\{[(\eta^5\text{-}C_5H_5)_2Co]_{1/4}TaS_2\}$ is typical.[1] As cobaltocene and chromocene have the lowest first ionisation potentials of the transition series metallocenes (5·56 and 5·71 eV respectively[2]) it may be that ready transfer of an electron from the organometallic guest to the host dichalcogenide is crucial in the formation of these compounds, as in the ionic alkali metal intercalates.[3]

Reactions were carried out by heating ZrS_2 powder (particle size $<50\,\mu m$) with a toluene solution of the sandwich compound in sealed ampoules at 400 K for 3 days. The formation of a new intercalation compound was detected by the changed appearance of the solid phase, its weight increase and elemental analysis, and *X*-ray powder diffraction. The data are summarised in the Table, which also includes data for $\{[(\eta^5\text{-}C_5H_5)_2Co]_{1/4}ZrS_2\}$.[1] These show that the three compounds containing $(\eta^5\text{-}C_5H_5)$ rings have stoicheiometries corresponding to $\frac{1}{4}$ guest molecule per formula unit, as found for the metallocene intercalates, whereas the bisarene-organometallic intercalates have stoicheiometries of $\frac{1}{6}$ or less.

The *X*-ray powder diffraction patterns of all the new intercalates could be fully indexed on the basis of an hexagonal cell with an expanded and tripled *c* axis. The patterns varied in peak width, as is reflected in the standard deviations of the *c* lattice parameters. It is interesting to note that the diffraction data are not consistent with a rhombohedral structure as the (106) reflection is strong and in this respect the intercalates resemble $LiHfS_2$, but not $LiZrS_2$; both these Li compounds have tripled *c* axes.[4] If it is considered that the guest sandwich molecules may be orientated with their principal molecular axis either (a) perpendicular or (b) parallel to the host layers then the observed constancy of the expansions for the bis-arene-molybdenum intercalates suggests configuration (a). However, for those compounds with at least one $(\eta^5\text{-}C_5H_5)$ ring the *c* axis expansion parallels the increasing diameter of the larger ring as would be expected for orientation (b); we note that all such intercalates have stoicheiometries corresponding to $\frac{1}{4}$ guest molecule per formula unit. The stoicheiometry found for $\{[(\eta^6\text{-}C_6H_6)_2Cr]_{1/6}ZrS_2\}$ suggests its inclusion with the molybdenum compounds in class (a).

Table

Organometallic intercalates of zirconium disulphide[a]

Guest[b]	I.P./ eV[c]	C% (wt.)[d]	Stoicheiometry, x[e]	c axis[f]/ Å	Lattice expansion /Å
$(bnz)_2Mo$	5·52	11·59	0·16	34·93(2)	5·81(1)
$(tol)_2Mo$	5·32	11·39	0·13	34·90(4)	5·80(1)
$(mes)_2Mo$	5·13	9·81	0·08	34·83(4)	5·78(2)
$(bnz)_2Cr$	5·4[h]	12·46	0·16	35·20(2)	5·90(1)
$(cp)_2Co$	5·56[i]				5·35[g]
$(cp)_2Cr$	5·71[i]	14·87	0·25	34·31(2)	5·61(1)
(bnz)(cp)Cr	6·20	15·67	0·24	35·70(2)	6·07(1)
(cht)(cp)Cr	5·59	17(3)	0·25	36·0(2)	6·17(7)
(cot)(cp)Ti	5·67	17·77	0·23	36·69(1)	6·40(1)

[a] ZrS_2 was synthesised from the elements and handled under nitrogen. The lattice parameters were $a = 3{\cdot}660(2)$ and $c = 5{\cdot}829(6)$ Å. [b] bnz = η^6-benzene, tol = η^6-toluene, mes = η^6-mesitylene, cp = η^5-cyclopentadienyl, cht = η^7-cycloheptatrienyl, and cot = η^8-cyclooctatetraene. [c] I.P. = first vertical ionisation potential, as measured by photoelectron spectroscopy. Values are taken from ref. 7 unless indicated otherwise. [d] The carbon content was determined by microanalysis of several samples. [e] The stoicheiometry was calculated from the carbon analysis, and confirmed in the case of $\{[(\eta^6\text{-}C_6H_6)_2Mo]\text{–}ZrS_2\}$ by sulphur (32·0%) and molybdenum (7·98%) analyses giving $S_2:Mo = 0{\cdot}17$. In the text x is rounded to $\frac{1}{6}$ (=0·167) or $\frac{1}{4}$ where appropriate. [f] The *c* axis was determined from a least-squares fit of the powder diffraction pattern. [g] Datum from ref. 1; preparation of the intercalate was repeated and the lattice expansion [derived from the (001) reflections] was confirmed. [h] From ref. 8. [i] From ref. 2.

We also note that the organometallic compounds which have been successfully intercalated all have ionisation potentials $< 6\cdot2$ eV and sandwich structures with parallel rings, and that all the corresponding sandwich cations are stable to isolation. Under similar conditions we were unable to prepare ZrS_2 intercalates of other 'electron rich' organometallic compounds, such as $[(\eta^8\text{-}C_8H_8)_2U]$ (1st I.P. 7·2 eV[5]), $[(\eta^6\text{-}C_6H_6)_2V]$ (5·2 eV[6]), $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ (6·4 eV[7]), and $[(\eta^5\text{-}C_5H_5)_2MoC_2H_4]$ (6·0 eV[7]). It seems therefore, that a low first ionisation potential for the guest molecule is not of itself a sufficient criterion for the formation of organometallic intercalates.

Finally we have observed oxidation of $\{[(\eta^5\text{-}C_5H_5)_2Co]_{1/4}\text{-}TaS_2\}$ by water at pH 5 to give parent 1T-TaS_2, $[(\eta^5\text{-}C_5H_5)_2\text{-}Co^+]$, and H_2 which suggests that organometallic intercalates may undergo reactions analogous to those of the hydrated alkali metal compounds of the dichalcogenides.[9] A consequent study of ion exchange of $\{K_{1/3}(H_2O)_{2/3}\ TaS_2\}$ with $[(C_6H_6)_2Cr^+]$ in alkaline aqueous solution showed that the new intercalate $\{[(\eta^6\text{-}C_6H_6)_2Cr]_{0.14}\text{-}TaS_2\}$ was formed. We were unable to make this compound by direct reaction between ZrS_2 and $[(\eta^6\text{-}C_6H_6)_2Cr]$, illustrating the importance of kinetic factors in intercalation reactions.

(*Received*, 12*th July* 1976; *Com.* 797.)

[1] M. B. Dines, *Science*, 1975, **188**, 1210.
[2] S. Evans, M. L. H. Green, B. Jewitt, G. H. King, and A. F. Orchard, *J.C.S. Farady II*, 1974, **70**, 356.
[3] W. Rudorff, *Chimia*, 1965, **19**, 489.
[4] M. S. Whittingham, and F. R. Gamble, *Mater. Res. Bull.*, 1975, **10**, 363.
[5] J. P. Clark, and J. C. Green, *J. Organometallic Chem.*, 1976, **112**, C14.
[6] S. Evans, J. C. Green, B. Higginson, and S. E. Jackson, *J.C.S. Dalton*, 1974, 304.
[7] J. C. Green, B. Higginson, and S. E. Jackson, *J.C.S. Dalton*, 1975, 403.
[8] S. Evans, J. C. Green, and S. E. Jackson, *J.C.S. Faraday II*, 1972, 301.
[9] R. Schöllhorn, E. Sick, and A. Lerf, *Mater. Res. Bull.*, 1975, **10**, 1005.