Intercalation of Redox-active Organometallic Cubane Clusters into Layered Metal Oxides and Related Solids

Kalyan Chatakondu, Malcolm L. H. Green, Jingui Qin, Mark E. Thompson, and Philip J. Wiseman

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.

The preparation and solid state properties of compounds formed by intercalation of redox-active cubane cluster compounds [Fe$_4$(η-C$_5$H$_4$Me)$_4$(μ^3-S)$_4$] and [Mo$_4$(η-C$_5$H$_4$Pr^i)$_4$(μ^3-Se)$_4$] into MoO$_3$ or FeOCl, and of related organometallic intercalation compounds, is described.

It has been shown that electron-rich organometallic sandwich compounds can intercalate into MX$_2$ (M = Ti, Zr, Hf, Nb, Ta; X = S, Se) and related layered host materials.[1] The cubane clusters [M$_4$(η-C$_5$H$_4$R)$_4$(μ^3-E)$_4$] (M = Fe, Cr, Mo; E = S, Se; R = H, Me, Pr^i) may be classed as electron-rich. For example, [Mo$_4$(η-C$_5$H$_4$Pr^i)$_4$(μ^3-S)$_4$] has a first ionization potential of 5.0 eV in the gas phase.[2] These clusters can undergo multiple reversible oxidation reactions forming stable cations.[2,3] Such compounds may be thought of as molecular analogues of highly electropositive atoms (*e.g.* sodium or magnesium). We were interested to explore this analogy and examine the possibility of preparing organometallic counterparts of molybdenum bronzes (molybdenum oxide–alkali metal intercalates).[4]

Treatment of molybdenum trioxide (particle size <60 µm) with [Fe$_4$(η-C$_5$H$_4$Me)$_4$(μ^3-S)$_4$] in acetonitrile at 100 °C results in intercalation of the cluster; thorough washing of the resulting solid with CH$_2$Cl$_2$ gives a shiny black compound of stoicheiometry {[Fe$_4$(η-C$_5$H$_4$Me)$_4$(μ^3-S)]$_4$}$_{0.15}$·MoO$_3$, (**1**). Microanalysis shows the stoicheiometry and confirms that the C : Fe ratio (6 : 0.95) remains unchanged upon intercalation. The first 5 lines of an 0*k*0 series indicate a layer spacing of at least 17.2 Å, which is 10.3 Å greater than the 6.9 Å spacing in MoO$_3$. Treatment of (**1**) with NaBF$_4$ causes displacement of the intercalated cation [Fe$_4$(η-C$_5$H$_4$R)$_4$(μ^3-S)$_4$]$^+$, which was isolated as the BF$_4^-$ salt; the other product was a solvated sodium bronze, [Na$_x$(H$_2$O)]$_y$·MoO$_3$. Further, oxidation of (**1**)

with bromine results in de-intercalation of [Fe$_4$(η-C$_5$H$_4$R)$_4$(μ^3-S)$_4$]$^+$ giving pure MoO$_3$. The intercalation reaction is solvent dependent. When MoO$_3$ is treated with [Fe$_4$(η-C$_5$H$_4$Me)$_4$(μ^3-S)$_4$] in 1,2-dimethoxyethane (DME) rather than acetonitrile, the MoO$_3$ turns black and analysis shows the material has the stoicheiometry {[Fe$_4$(η-C$_5$H$_4$Me)$_4$(μ^3-S)$_4$]}$_x$·MoO$_3$, x = 0.10. However, powder X-ray diffraction data show that *no* intercalation has occurred. A diagrammatic representation of (**1**) is shown in Figure 1.

The compound [Fe$_4$(η-C$_5$H$_4$Me)$_4$(μ^3-S)$_4$] was intercalated into a large crystal of MoO$_3$ (5 × 2 × 0.15 mm^3) giving the intercalate (**1**), x = 0.15 (determined by C and H analysis of a portion of the crystal). The crystal had a substantial conductivity of 0.6 ± 0.5 (Ω cm)$^{-1}$ along the long crystal axis, while the conductivity along the shortest axis (the interlayer direction) is lower by two orders of magnitude.

The question arises as to whether the cluster cations in (**1**) have a charge of +1, +2, or more, or whether there could be more than one charged species. It is unlikely that the cluster is dicationic, since we do not observe a signal in the solid state n.m.r. spectrum for the intercalated cluster as would be expected for a paramagnetic monocation. Also, when treated with NaBF$_4$ the cluster bronze compound gives the mono-cationic salt [Fe$_4$(η-C$_5$H$_4$Me)$_4$(μ^3-S)$_4$]$^+$BF$_4^-$.

We have synthesised other cubane intercalation compounds as shown in Table 1, which were all characterised by elemental analysis and X-ray powder diffraction. In some cases it was

Table 1. New intercalation compounds.

Compound	Layer expansion,[d] /Å	Conditions of synthesis[c] Solvent	θ/°C, t/day
(1) $[Fe_4(\eta\text{-}C_5H_4Me)_4\text{-}(\mu^3\text{-}S)_4]_{0.15}\cdot MoO_3$[a]	10.3	MeCN	100, 3
(2) $[Mo_4(\eta\text{-}C_5H_4Pr^n)_4\text{-}(\mu^3\text{-}Se)_4]_{0.05}\cdot MoO_3$[b]	15.2	MeCN	100, 30
(3) $[Fe_4(\eta\text{-}C_5H_4Me)_4\text{-}(\mu^3\text{-}S)_4]_{0.08}\cdot FeOCl$	9.1	DME	20, 8
(4) $[Cr_4(\eta\text{-}C_5H_4Me)_4\text{-}(\mu^3\text{-}S)_4]_{0.10}\cdot FeOCl$	8.6	DME	20, 40
(5) $[Fe(\eta\text{-}C_5H_4CH_2CH_2NH_2)\text{-}(\eta\text{-}C_5H_5)]_{0.6}\cdot MoO_3$	14.5	MeCN	100, 6
(6) $[Fe(\eta\text{-}MeC_5H_4CH_2CH_2NH_2)\text{-}(\eta\text{-}C_5H_4Me)]_{0.5}\cdot MoO_3$	15.5	MeCN	100, 5
(7) $[Fe(MeC_5H_3CH(OH)CH_2NH_2)\text{-}(\eta\text{-}C_5H_4Me)]_{0.4}\cdot MoO_3$	14.8	MeCN	100, 8
(8) $[Fe(\eta\text{-}C_5H_4CH_2CH_2NH_3)\text{-}(\eta\text{-}C_5H_5)]^{2+}_{0.6}\cdot Zr(HPO_4)_2(PO_4)$	14.1	EtOH	20, 3h
(9) $[Ir(PMe_3)_4H]_{0.15}\cdot ZrS_2$[b]	9.2	Toluene	140, 12
(10) $[Mo(\eta\text{-}C_5H_5)_2H_2]_{0.08}\cdot FeOCl$	5.6	DME	20, 4
(11) $[Co(\eta\text{-}C_5H_5)_2]_{0.66}\cdot MoO_3$	5.8	MeCN	100, 7

[a] Paramagnetic, $\mu = ca.$ 1.5 μ_B [b] X-Ray data show that the material is not fully intercalated. [c] Samples were in a glass ampoule *in vacuo*, and heated in an oil bath. [d] The values given are lower limits as at this stage. We have assumed retention of the original symmetry of the host unit cell upon intercalation. The expansion may be slightly larger if the intercalates exhibit monoclinic or lower symmetry.

found that the use of ultrasound caused a substantial reduction in the reaction times, as noted elsewhere for other intercalation reactions.[5]

Cobaltocene is a very strong reducing agent (I.P. 5.35 eV; $E^{+/0}$ −0.945 V[10]); thus we found it surprising that it would not react with MoO_3 to give an intercalation compound. Treatment of MoO_3 with an acetonitrile solution of cobaltocene gives a blue/black material which analyses as $[Co(\eta\text{-}C_5H_5)_2]_{0.11}\cdot MoO_3$, but powder X-ray diffraction indicates that no intercalation has occurred. Similarly, if DME is used as the reaction solvent a blue-black unintercalated material is obtained, $[Co(\eta\text{-}C_5H_5)_2]_{0.16}\cdot MoO_3$. However, when MoO_3 is treated with an acetonitrile solution of cobaltocene together with an equimolar amount of $[Co(\eta\text{-}C_5H_5)_2]PF_6$, a black compound is obtained of stoicheiometry $[Co(\eta\text{-}C_5H_5)_2]_{0.66}\cdot MoO_3$ (1), which X-ray analysis shows is an intercalated material. The first six lines of an 0k0 series indicate an expansion in the interlayer spacing of at least 5.85 Å. This expansion is larger than that observed for $[Co(\eta\text{-}C_5H_5)_2]_{0.16}\cdot FeOCl$ (4.9 Å)[6] or $[Co(\eta\text{-}C_5H_5)_2]_{0.29}\cdot MX_2$ (5.2—5.4 Å).[1] Treatment of (2) with $NaBF_4$ caused de-intercalation giving $[Co(\eta\text{-}C_5H_5)_2]BF_4$.

Ferrocene will intercalate into FeOCl;[6] however, it will not intercalate into 1T TaS_2 or MoO_3. This may be attributed to the greater oxidising ability of FeOCl. The intercalation of organoamines into layered compounds such as 2H TaS_2 and MoO_3 is well known.[7,8] We, therefore, prepared a range of amino-ferrocenes in the expectation that the amine functionality would promote intercalation. We have found that the amino-ferrocenes readily intercalate into MoO_3, both as a powder and as single crystals, to give shiny black intercalates; the characterising data are given in Table 1. The monoamino-ferrocenes form bi-layers, as indicated by stoicheiometry and
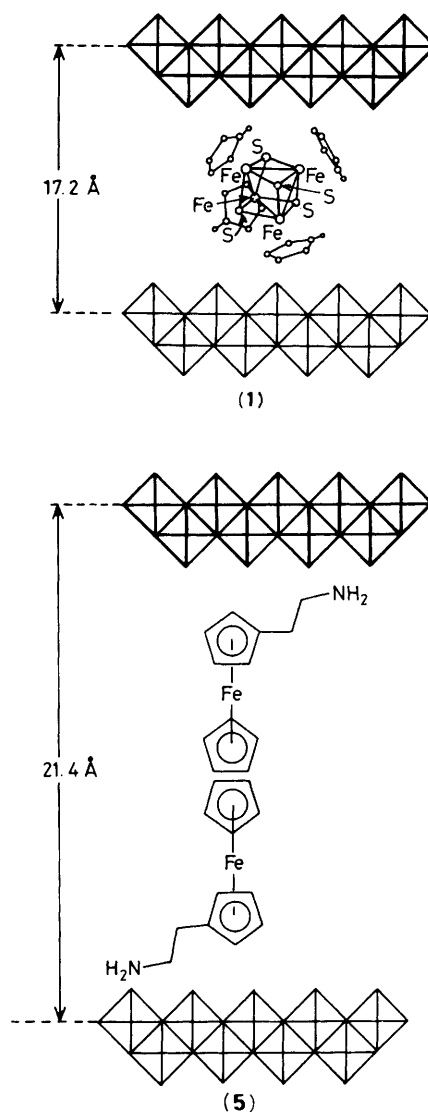

Figure 1. Representations of the structures of the intercalates (1) and (5).

the large inter-layer separations; the racemic ferrocene $Fe(MeC_5H_3CH(OH)CH_2NH_2)(MeC_5H_4)$ was also readily intercalated. A representation of the structure of $[Fe(\eta\text{-}C_5H_4CH_2CH_2NH_2)(\eta\text{-}C_5H_5)]_{0.6}\cdot MoO_3$ (5), is given in Figure 1.

The mono-amino-ferrocene $[Fe(\eta\text{-}C_5H_4CH_2CH_2NH_2)(\eta\text{-}C_5H_5)]$ intercalates readily into $[d\text{-}Zr(HPO_4)_2\cdot H_2O]$ giving $[Fe(\eta\text{-}C_5H_4CH_2CH_2NH_3)(\eta\text{-}C_5H_5)]^{2+}_{0.6}\cdot Zr(HPO_4)_2(PO_4)$ (8). The solid-state [13]C n.m.r. spectrum of (8) compares closely with that of the hydrochloride salt of the parent amino-ferrocene. This suggests that in (8) the intercalated species is the alkylammonium cation $[Fe(\eta\text{-}C_5H_4CH_2CH_2NH_3)(\eta\text{-}C_5H_5)]^{+}$.

The compounds $[Ir(PMe_3)_4H]$ and $[Mo(\eta\text{-}C_5H_5)_2H_2]$ are strong bases; for example, they are readily protonated. These compounds may be thought of as inorganic analogues of organo-amines. Treatment of ZrS_2 with $[Ir(PMe_3)_4H]$ gives the intercalate compound $[Ir(PMe_3)_4H]_{0.15}\cdot ZrS_2$ (9), with an inter-layer expansion which is consistent with an estimated diameter for $[Ir(PMe_3)_4H]$ of 9 Å. Treatment of (9) with $NaBPh_4$ in tetrahydrofuran (THF) results in ion exchange giving $[Ir(PMe_3)_4H]BPh_4$ and the sodium ion-ZrS_2 intercalate.

Treatment of FeOCl with $[Mo(\eta\text{-}C_5H_5)_2H_2]$ gives the intercalate $[Mo(\eta\text{-}C_5H_5)_2H_2]_{0.08}\cdot FeOCl$ in which the expansion is 5.6 Å.

During the course of this work the cluster intercalate $[Fe_6S_8(PEt_3)_3]_{0.05}\cdot TaS_2$ was reported. It was prepared as a thin film from TaS_2 dispersions.[9]

In conclusion, we have extended the range of organometallic intercalation compounds including the cluster bronzes and shown that organometallic compounds with basic centres can be intercalated into a variety of host lattices.

References

1 M. B. Dines, *Science*, 1975, **188**, 1210.
2 J. A. Bandy, C. E. Davis, J. C. Green, M. L. H. Green, K. Prout, and D. P. S. Rodgers, *J. Chem. Soc., Chem Commun.*, 1983, 1395.
3 T. Toan, B. K. Teo, J. A. Ferguson, T. J. Meyer, and L. F. Dahl, *J. Am. Chem. Soc.*, 1977, **99**, 408.
4 M. S. Whittingham and A. J. Jacobson, 'Intercalation Chemistry,' Academic Press, New York, 1982.
5 K. Chatakondu, M. L. H. Green, M. E. Thompson, and K. S. Suslick, *J. Chem. Soc., Chem. Commun.*, 1987, 900.
6 T. R. Halbert and J. Scanlon, *Mater. Res. Bull.*, 1979, **14**, 415.
7 F. R. Gamble, J. M. Osieki, M. Cais, R. Pisharody, F. J. Disalio, and T. H. Geballe, *Science*, 1971, **174**, 493.
8 P. G. Dickens and S. J. Hibble, *Solid State Ionics*, 1986, **22**, 69.
9 L. F. Nazar and A. J. Jacobson, *J. Chem. Soc., Chem. Commun.*, 1986, 570.
10 U. Koelle, *J. Organomet. Chem.*, 1978, **152**, 225.