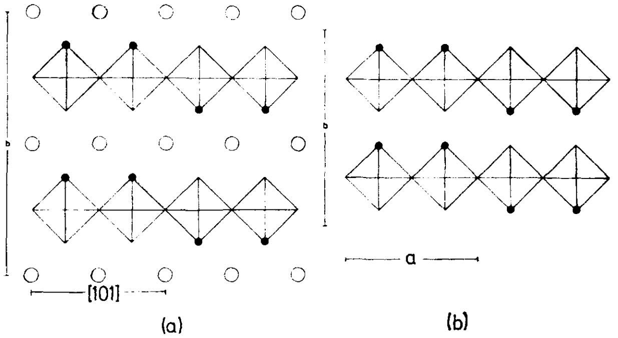
On the Feasibility of forming Organic Intercalates from the Layered Solid $(MoO_3{\cdot}OH_2)_n$

By **John M. Adams** and **John R. Fowler**, Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE

Attempts to intercalate some small polar molecules between the $(MoO_3{\cdot}OH_2)_n$ layers of partially dehydrated $MoO_3{\cdot}2OH_2$ are described, as are characteristic data for two new complexes of MoO_3 with methanol and formamide.

INTEREST in the preparation and properties of new intercalates is, at present, considerable; and apart from the exploration of novel features of the chemistry of such complexes derived from widely known layered host solids such as graphite,[1-3] sheet silicates,[4-6] and transition-metal chalcogenides,[7] there is merit in utilizing hitherto unexamined types of layered hosts with a view to uncovering new classes of extended (sandwiched) donor–acceptor complexes. One possible potentially interesting host is the monohydrate of MoO_3, formed, as described below, by the partial dehydration of $MoO_3{\cdot}2OH_2$.

The crystal structure of yellow $MoO_3{\cdot}2OH_2$ has been shown by Krebs [8] to consist of infinite $(MoO_3{\cdot}OH_2)_n$ layers which are stacked normal to the crystallographic *b* axis. Five oxygens and one co-ordinated water molecule form a strongly distorted octahedron around every molybdenum. An interesting feature of this hydrate is the occurrence of a second type of water molecule, not directly bonded to molybdenum: it occupies the interlayer region and forms hydrogen bonds linking the two neighbouring layers (see Figure). The dihydrate may be readily converted into the monohydrate on moderate heating and, as the loosely held water is lost, the layers are stabilized by the movement of every second layer by $a/4 + c/4$.[8,9] This partial dehydration is topotactic.[9] The possibility therefore exists of forming stable intercalates when suitable guest species are introduced to the monohydrate host, consisting of layers of $(MoO_3{\cdot}OH_2)_n$. The polar species chosen for this brief exploratory study were those known to form stable intercalates with the layered silicates kaolinite and montmorillonite,[4,5,10] there being, in each case, a loose kinship between the oxygen and 'hydroxyl' moieties bonded to the six co-ordinated metal atoms (Al or Mo) situated in the extended sheets of kaolinite and $(MoO_3{\cdot}OH_2)_n$.



Comparison of the schematic structures involved in the topotactic dehydration of $MoO_3{\cdot}2OH_2$: filled circles, co-ordinated H_2O; empty circles, interlayer H_2O. (a) $(\bar{1}01)$ projection of $MoO_3{\cdot}2OH_2$, the octahedra being $[MoO_5(OH_2)]$; (b) (001) projection of $MoO_3{\cdot}OH_2$ (proposed), the octahedra being $[MoO_5(OH_2)]$ (after Günter [9])

EXPERIMENTAL

Yellow molybdenum oxide dihydrate was prepared by the method of Carpeni [11] from molybdenum oxide obtained from George and Becker Ltd., although the crystallization time required was much longer than that indicated. The yellow form of molybdenum oxide monohydrate was prepared from the dihydrate by heating in air at 80 °C for several hours. The *X*-ray diffraction pattern was in excellent agreement with the data of Günter.[9] Intercalation was attempted using both the monohydrate and dihydrate as starting materials. The simple procedure consisted of shaking the hydrate with the compound in question for a period of time up to one week at room temperature. At the end of that time the hydrate was filtered off, allowed to dry in air, and an *X*-ray powder photograph was taken using an XDC-700 Guinier-Hägg camera.

RESULTS AND DISCUSSION

In most cases (with tetrahydrofuran, tetrahydropyran, monochloracetic acid, ethanediamine and 1,4-dioxan) no obvious reaction occurred between the organic compound and the MoO_3 hydrates. However, in four cases there was immediate and obvious reaction although in two of these the products did not give a diffraction pattern, probably because of small particle size. Hydrazine hydrate gave a brown material which could well have contained molybdenum metal in view of

---

[1] N. Ichikawa, T. Kondo, K. Kawase, M. Sudo, T. Onishi, and K. Jamaru, *J.C.S. Chem. Comm.*, 1972, 176.

[2] A. Marchand in 'Chemistry and Physics of Carbon,' ed. P. L. Walker, jun., Arnold, London, 1971, vol. 7.

[3] J. M. Thomas, *Phil. Trans. Roy. Soc.*, 1974, **A227**, 251.

[4] A. Weiss in 'Organic Geochemistry,' eds. G. Eglington and M. J. T. Murphy, Springer-Verlag, New York, 1969.

[5] D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and (in part) J. O. Williams, *J.C.S. Dalton*, 1974, 2207.

[6] M. J. Tricker, D. T. B. Tennakoon, J. M. Thomas, and S. H. Graham, *Nature*, 1975, **253**, 110.

[7] G. S. Parry, C. B. Scruby, and P. M. Williams, *Phil. Mag.* 1974, **29**, 601.

[8] B. Krebs, *Chem. Comm.*, 1970, 50.

[9] J. R. Günter, *J. Solid State Chem.*, 1972, **5**, 354.

[10] 'X-ray Identification and Crystal Structures of Clay Minerals', ed. G. Brown, Mineralogical Society, London, 1961.

[11] G. Carpeni, *Bull. Soc. chim. France*, 1947, 484.

the reducing properties of this compound, whereas absolute ethanol with the dihydrate yielded a dark blue solution which, on evaporation of excess ethanol, gave a blue-black pseudocrystalline product. Reaction with methanol and formamide was, however, more fruitful since the products could be investigated by *X*-ray diffraction. Methanol with $MoO_3{\cdot}OH_2$ gave a colour change from yellow to white in part of the hydrate sample; the weak diffraction pattern was that of $MoO_3{\cdot}OH_2$. Methanol with $MoO_3{\cdot}2OH_2$ gave a white powder which turned blue on filtration. This product possessed a diffraction pattern different from that of the dihydrate (Table 1) and analysis figures of 6.75% C, 1.95% H suggest $MoO_3{\cdot}(CH_3OH)$ but it is to be noted that the hydrogen percentage is lower than expected by some 15%. Formamide with either of the hydrates gave a white powder, the diffraction pattern of which was distinct from both mono- and dihydrate diffraction patterns (Table 1); it was also different from the methanol–molybdenum dihydrate pattern. Analysis results of 9.5% C, 2.45% H, 11.1% N correspond to $MoO_3{\cdot}(OH_2)_{0.08}(HCONH_2)_{1.79}$. Since the diffraction pattern had weak traces of lines due to $MoO_3{\cdot}2OH_2$ we may convert the above formula into $(MoO_3{\cdot}2OH_2)_{0.04}(MoO_3)_{0.96}(HCONH_2)_{1.79}$, *i.e.* we have prepared a new product of approximate composition $MoO_3{\cdot}(HCONH_2)_{1.86}$ which is reasonably close to $MoO_3{\cdot}2HCONH_2$.

TABLE 1

d-Spacings (in Å) for methanol and formamide products

$MoO_3{\cdot}CH_3OH$	$MoO_3{\cdot}2HCONH_2$
7.86s	13.89w
5.54m	11.04w
5.48m	9.63w
4.65m	8.79w
4.19m	6.25s
3.90w	5.91s
3.54m	3.54s
3.44w	3.44s
3.06m	3.21s
	2.90m
	2.85w
	2.78w
	2.66m
	2.62w
	2.60w
	2.29m
	2.21w
	1.98m
	1.78w
	1.75w

A compound of formula $MoO_3{\cdot}2CH_3OH$ has been prepared by Krauss and Huber[12] by stirring powdered $MoO_2{\cdot}2OH_2$ with absolute methanol at 60 °C. Methanol was lost from this sample under vacuum at 20 °C. The i.r. spectrum of this compound is compared with that of $MoO_3{\cdot}CH_3OH$ in Table 2. It may be noted that the absorptions for methanol and formamide have been shifted slightly in the compound from their value in the liquid due to the constraints imposed by the formation of the compound. In the case of the formamide compound new absorptions appear at 920, 935, and 650 nm.

TABLE 2

I.r. spectra (in cm^{-1})

$MoO_3{\cdot}2CH_3OH$[6]	Methanol	$MoO_3{\cdot}CH_3OH$
3 239s	3 400s	3 300s
2 922m	2 940m	2 960w
2 817m	2 820m	2 920w
1 449w	1 450m	1 450m
1 382w	1 410m	1 380m
1 100w	1 115w	1 090m
998m	1 030s	1 050m

Formamide	$MoO_3{\cdot}HCONH_2$
3 320s	3 320s
2 970w	2 960w
2 880w	2 910w
1 690s	1 660s
1 600w	1 570w
1 445w	1 445w
1 385s	1 360w
1 305s	1 325w
1 085s	1.095s
1 045s	1 040s
	935s
	920s
875w	875s
695w	695w
	650s

Further study is required before the structure of the two new compounds can be ascertained. It may be concluded, however, that simple organic molecules which are rather tenaciously retained between the sheets of montmorillonite do not form intercalates with $(MoO_3{\cdot}OH_2)_n$.

We thank the S.R.C. for the Advanced Course Studentship (to J. R. F.) during the tenure of which this work was carried out. The investigation was suggested by Professor J. M. Thomas.

[5/1297 *Received*, 1*st July*, 1975]

---

[12] H. L. Krauss and W. Huber, *Chem. Ber.*, 1961, **94**, 2864.