Synthesis and ^{17}O N.M.R. Structure Determination of a η-Cyclopentadienyl Titanomolybdate, $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$

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Summary Reaction of $[(\eta\text{-}C_5H_5)_2TiCl_2]$ with $(Bu^n_4N)_2[Mo_2O_7]$ and water in CH_2Cl_2 yields $(Bu^n_4N)_3[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]$, shown to contain the $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ anion which is related to the octahedral $Mo_6O_{19}{}^{2-}$ anion by replacement of an $[Mo^{VI}O]^{4+}$ sub-unit by $[Ti^{IV}(\eta\text{-}C_5H_5)]^{3+}$.

The unusual stability of the recently reported α-$[(\eta\text{-}C_5H_5)Ti(PW_{11}O_{39})]^{4-}$ anion[1] has prompted us to attempt the synthesis of related compounds which contain the same organometallic sub-unit bonded to different polyoxoanion clusters. The complex described here, the $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ anion, demonstrates the critical role of the polyoxoanion ligand in determining the stability of polyoxoanion supported organometallics.

The $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ anion is synthesized as a

$$2[(\eta\text{-}C_5H_5)_2TiCl_2] + 5[Mo_2O_7]^{2-} + H_2O \rightarrow 2[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-} + 4Cl^- + 2C_5H_6 \quad (1)$$

tetrabutylammonium salt according to equation (1). Slow addition of $[(\eta\text{-}C_5H_5)_2TiCl_2]$ in dry CH_2Cl_2 to a dry CH_2Cl_2 solution of $(Bu^n_4N)_2[Mo_2O_7]^{2-}$ followed by addition of moist toluene and slow evaporation of solvent in an argon atmosphere yields crystalline, solvated product. These crystals, upon drying *in vacuo*, crumble to a yellow powder formulated as $(Bu^n_4N)_3[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]$ (**1**) according to elemental analysis and the relative intensities (1 : 5·4) of ^1H n.m.r. resonances in CD_2Cl_2 for the C_5H_5 protons and the counterion $N\text{-}CH_2$ protons.

Table. 13·5 MHz ^{17}O Pulse Fourier transform n.m.r. chemical shift data

Anion	Chemical shifts[a] OV	 OMo	 OMoV or OMoTi	 OMo_2	 OM_6
$[Mo_6O_{19}]^{2-}$ [b]		927		559	−32
$[VMo_5O_{19}]^{3-}$ [c]	1200[d]	885	665[d]	541 531	−22
$[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ [e]		863 834	641	535 516	5

[a] Positive chemical shift in p.p.m. downfield from pure H_2O at 25 °C, ±3 p.p.m. unless otherwise indicated. [b] Data from ref. 3. [c] $(Bu^n_4N)_3[VMo_5O_{19}]$, 10% ^{17}O, 0·08 M in MeCN at 80 °C. [d] ±5 p.p.m. [e] $(Bu^n_4N)_3[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]$, 19% ^{17}O, 0·23 M in MeCN at 25 °C.

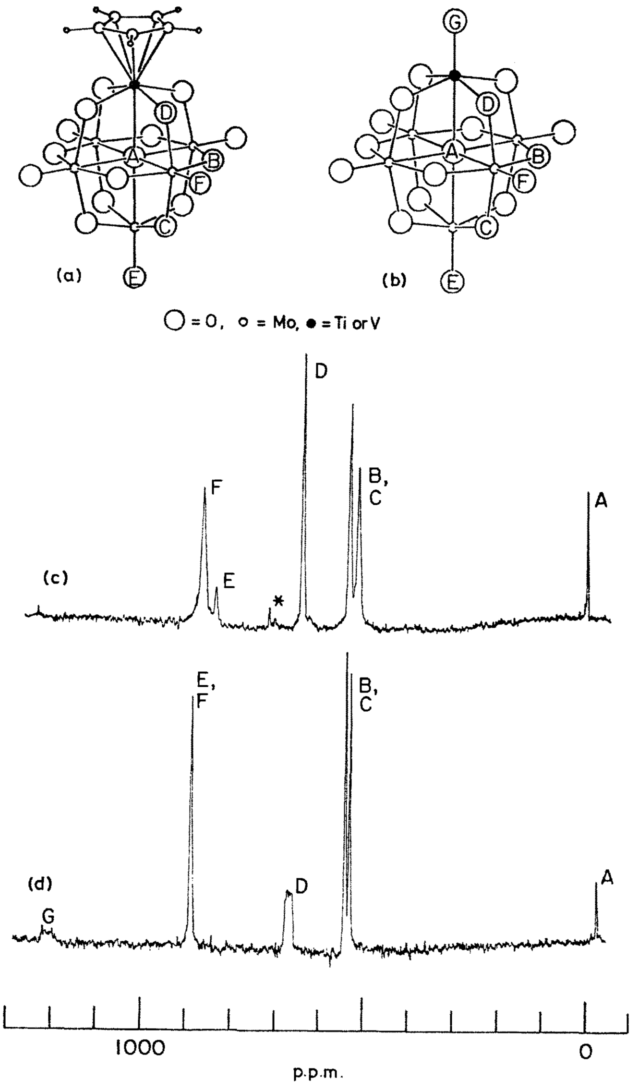

Figure. (a) Proposed structure of $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ and (b) structure of $[VMo_5O_{19}]^{3-}$. One member of each symmetry equivalent set of oxygen atoms is labelled, assuming free rotation of the C_5H_5 ligand in (a). This labelling is used to assign resonances in the ^{17}O n.m.r. spectra of (c) $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ and (d) $[VMo_5O_{19}]^{3-}$. The asterisk in (c) identifies a resonance arising from a small amount of sample decomposition. See Table for spectral data.

The structure of the $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ anion shown in Figure (a) is proposed on the basis of the completely resolved ^{17}O n.m.r. spectrum shown in Figure (c). The spectral assignments given in the Table and Figure (c) were obtained by comparison of the spectrum of (**1**) with the spectrum of $(Bu^n_4N)_3[VMo_5O_{19}]$† which contains the structurally related $[VMo_5O_{19}]^{3-}$ anion [see Figure (b) and (d)]. Although the O_B and O_C resonances for (**1**) cannot be uniquely assigned to the 535 and 516 p.p.m. resonances, the O_E and O_F resonances can be uniquely assigned using intensity arguments. The resonances for the $[VMo_5O_{19}]^{3-}$

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† Prepared by stoicheiometric addition of methanolic Bu^n_4NOH to V_2O_5 and α-$(Bu^n_4N)_4[Mo_8O_{26}]$ in MeCN. Elemental analysis and i.r. spectroscopy in the 650—1000 cm^{-1} region show that this compound contains the $[VMo_5O_{19}]^{3-}$ anion which is isostructural with the $[VW_5O_{19}]^{3-}$ anion: C. M. Flynn, Jr. and M. T. Pope, *Inorg. Chem.*, 1971, **10**, 2524.

anion were assigned using chemical shift data for the $[Mo_6O_{19}]^{2-}$ anion[3] (see Table), following the same procedures as previously described[4] to assign the resonances for the $[VW_5O_{19}]^{3-}$ anion.

In contrast with the α-$[(\eta\text{-}C_5H_5)Ti(PW_{11}O_{39})]^{4-}$ anion, the $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ anion is decomposed by atmospheric moisture in the solid or solution state. Since the titanium co-ordination geometry is very similar in the two complexes, this difference in stability cannot be attributed to steric factors at the titanium site.

We thank the National Science Foundation and the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research, the Alfred P. Sloan Foundation for a Fellowship (to W. G. K.), and Mr. I. Miura for measuring the ^{17}O n.m.r. spectra.

(*Received, 14th August* 1978; *Com.* 885.)

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