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**True Nature of
Trihalotris(tetrahydrofuran)molybdenum(III),
MoX₃(THF)₃ (X = Cl, Br, I). A Paramagnetic ¹H
Nuclear Magnetic Resonance Study[†]**

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MoCl₃(THF)₃ is extensively used for the synthesis of molybdenum complexes in the III and lower oxidation states.¹⁻⁵ Several improved preparation procedures⁶⁻⁸ have been subsequently published after the original report.⁹ However, its structural nature

[†] Dedicated to Prof. Fausto Calderazzo on the occasion of his 60th birthday.

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Table I. Assignment of Paramagnetic ^1H Nuclear Magnetic Resonance δ Values to Structures I–IV^a

	I (α)	I (β)	II (α)	II (β)	III (α)	III (β)	IV (α)	IV (β)
X = Cl	65.7 (2)	8.2 (2)	25.0	3.7	6.73 (2)			
	56.2 (1)	6.1 (1)	17.9	3.4	6.49 (1)	2.34	6.2–6.0	2.34
X = Br	72.2 (2)	9.5 (2)	ca. 69	?	7.21 (2)			
	57.3 (1)	6.3 (1)	ca. 51	?	6.62 (1)	2.44	7.2–6.6	2.44

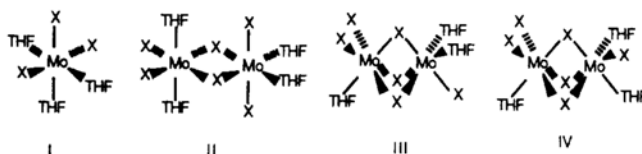
^aSee text for structures. Numbers in parentheses within each class are relative intensities.

has never been fully addressed, probably because of its insolubility in most solvents and its paramagnetism.²⁷ Recently, multigram-scale preparations of the analogous $\text{MoX}_3(\text{THF})_3$ (X = Br, I) compounds have appeared.^{10,11} A single-crystal structural study of the iodide derivative shows an octahedral meridional arrangement of the ligands.^{11,27} Structural studies of other MoX_3L_3 derivatives (X = Cl, Br, I; L = two-electron neutral donor) are limited to those few instances where single crystals suitable for X-ray diffraction have been obtained.^{3b,5,10b,12} NMR investigations have not been reported, and EPR studies are difficult.¹³

We have discovered that octahedral Mo(III) complexes containing phosphine ligands exhibit relatively sharp, paramagnetically shifted ^1H NMR spectra, which allow for the first time an assessment of their structure *in solution*.¹⁴ Paramagnetic NMR¹⁵ studies of mononuclear octahedral d^3 systems are limited to a few compounds of chromium(III) and vanadium(II) and one compound of tungsten(III).¹⁶ We have utilized this technique to investigate the nature of the tris(tetrahydrofuran) adducts of molybdenum(III) halides and have found an unexpectedly complex behavior. This communication reports the first paramagnetic ^1H NMR study of mononuclear molybdenum(III) coordination compounds, detailing the previously unknown chemical nature and behavior in solution of $\text{MoX}_3(\text{THF})_3$ (X = Cl, Br), and the results of a preliminary kinetic investigation of their decomposition.

The ^1H NMR spectrum of a CD_2Cl_2 solution of crystalline $\text{MoCl}_3(\text{THF})_3$ changes with time, and the initial pale purple solution deepens over time to a dark purple. A similar behavior was observed for the corresponding tribromide compound, where the color changes from orange to dark purple. The triiodide compound is not soluble enough in CD_2Cl_2 for an NMR study to be carried out, and the only resonances we could identify were those of free THF. The NMR peaks can be assigned to the compounds whose structures are illustrated in I–IV as shown in Table I. Free THF has resonances at δ 3.9 for the α -H and at

δ 2.0 for the β -H atoms. In both cases (X = Cl, Br), the monomer resonances decrease in intensity with time. The edge-sharing bioctahedral dimer II is noticeable in the early part of the experiment. For X = Cl, it initially increases to a maximum of 19% of the total molybdenum concentration after ca. 6 min at 30 °C, but subsequently disappears. For X = Br, there is much less of compound II produced initially, and its decay is more rapid than for X = Cl. Compounds III and IV increase in concentration throughout the experiment, as does free THF.



The assignments appear reasonable in view of the following. Higher paramagnetic shifts are expected for the mononuclear I ($S = 3/2$) than for II (for which metal–metal bonding or anti-ferromagnetic coupling can lower the effective magnetic moment) than for III and IV (where the closer approach of the two metals can give rise to a stronger metal–metal interaction). The observed shifts indicate, however, that even III and IV have residual paramagnetism. This is consistent with the available data from the literature and from other unpublished work of ours: although several edge-sharing bioctahedral compounds have short metal–metal separations (in the range 2.73–2.79 Å) and are diamagnetic,^{17–19} the recently reported²⁰ $\text{Mo}_2\text{Cl}_6(\text{PEt}_3)_4$ compound exhibits a long metal–metal separation (3.730 (1) Å) and a high magnetic moment. Concerning confacial bioctahedral compounds, the known $[\text{Mo}_2\text{X}_7(\text{PMe}_3)_2]^-$ ions (X = Cl,²¹ I²²) show a slight paramagnetic shift for the PMe_3 proton resonance, and we have observed similar shifts for the $\text{Mo}_2\text{Cl}_6\text{L}_3$ neutral complexes (L = PEt_3 , PMe_2Ph).¹⁴ The assignment of structure II to the edge-sharing bioctahedral dimer results primarily from the observation of two resonances for the α protons. An all-axial or all-equatorial derivative should exhibit only one signal. Although we cannot exclude that a mixture of all-axial and all-equatorial isomers is present (in which case they must react at approximately the same rate), we favor the structural assignment shown in II on the basis of other known structures of edge-sharing bioctahedral derivatives of molybdenum²⁰ and other metals.^{23,24} The α protons for the bromide analogue are much more paramagnetically shifted and indicate that II (X = Br) is almost as paramagnetic as I, whereas the metal–metal interaction in II (X = Cl) is substantial. The position of the β -H resonances for II (X = Br) could not be identified because the compound never accumulates to a sufficient

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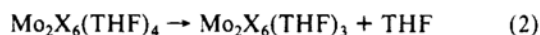
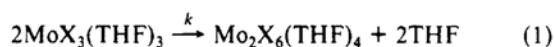
extent and because these peaks probably overlap with the β -H resonances of I and with the α -H resonances of III and IV. The stereoisomerism suggested for the confacial bioctahedral structure is analogous to that reported for the $[\text{Mo}_2\text{X}_7(\text{PMe}_3)_2]^-$ (X = Cl, I) ions.^{21,22}

The following points are also worthy of note. There is no extra peak in the NMR spectrum that could be assigned to a mononuclear facial isomer. Therefore, the $\text{MoX}_3(\text{THF})_3$ compounds are present *in solution* as meridional isomers exclusively. Integration establishes that the amounts of free THF and THF of compounds III and IV that are produced are equivalent to each other and correspond to 1.5 mol per mole of $\text{MoCl}_3(\text{THF})_3$ consumed. However, extrapolation of the data to zero time shows that the starting materials were already contaminated by free THF (for X = Cl, Br) and face-sharing dimers (for X = Cl).

An important point emerges from the latter observation. Most of the recommended procedures for the synthesis of $\text{MoCl}_3(\text{THF})_3$ involve the use of CH_2Cl_2 as solvent or cosolvent for the synthesis or separation procedure.^{1b,6,7} The product has been described before as orange, brownish-orange, pink, pinkish-purple, and even blue-purple.^{1b,2c,6,7,9} We propose that these different colors are the result of variable amounts of dinuclear impurities. According to our study, the product can be expected to be a mixture of $\text{MoCl}_3(\text{THF})_3$ and $\text{Mo}_2\text{Cl}_6(\text{THF})_3$, containing perhaps minor amounts of $\text{Mo}_2\text{Cl}_6(\text{THF})_4$ and free THF. Wedd and co-workers^{1b} reported that $\text{MoCl}_3(\text{THF})_3$ loses THF in benzene to afford a pinkish-red, diamagnetic solid, which they formulated as $\text{Mo}_3\text{Cl}_6(\text{THF})_5$ on the basis of analytical data. A subsequent investigation by electronic spectroscopy suggested that association to $\text{Mo}_2\text{Cl}_6(\text{THF})_3$ occurs instead.²⁵ The conversion of III and IV back to $\text{MoCl}_3(\text{THF})_3$ in THF is very slow (less than 20% conversion over 48 h at room temperature).

The above NMR data can be interpreted in terms of the two-step process illustrated in Scheme I. A preliminary kinetic analysis for the bromide system indicates a second-order decay of the monomer concentration, for a k value of $0.431 \pm 0.005 \text{ M}^{-1} \text{ min}^{-1}$ at 30 °C. The data for the chloride system are less accurate,

Scheme I



but the two halide systems take approximately the same time to transform to the final dinuclear product. More kinetic studies are planned for the near future.

Similar equilibria might take place with different ligand systems. For instance, the acetonitrile derivatives $\text{MoCl}_3(\text{MeCN})_3 \cdot \text{MeCN}$,⁸ $\text{MoCl}_3(\text{MeCN})_3$,⁹ and $\text{Mo}_2\text{Cl}_6(\text{MeCN})_3$ ²⁶ have all been described. We are planning to reinvestigate these compounds as well as others and to study the monomer/dimer interconversion by paramagnetic ¹H NMR.

Acknowledgment. We are grateful to the University of Maryland, College Park (UMCP), Department of Chemistry and Biochemistry, the UMCP General Research Board, the Camille and Henry Dreyfus Foundation (for a Distinguished New Faculty Award to R.P.), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. H.D.M. thanks the UMCP office of Undergraduate Studies for a Senior Summer Fellowship.

Supplementary Material Available: A figure showing the linear relationship between the inverse concentration of $\text{MoBr}_3(\text{THF})_3$ and time (1 page). Ordering information is given on any current masthead page.

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