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The Chemistry of Molybdenum and Tungsten. Part XIV. Oxomolybdenum(V) Complexes of Quinolines

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Oxomolybdenum(V) complexes of substituted hydroxyquinolines and quinolines have been obtained by the reaction of $MoOCl_3(THF)_2$ (THF = tetrahydrofuran) with 8-hydroxyquinolidine, isoquinoline, 3-methylisoquinoline, 6-methylquinoline, 7-methylquinoline, 5,6-benzoquinoline, 8-mercaptoquinoline and 2,2'-biquinolyl. Various types of complexes have been isolated ranging from the simple substitution of two THF ligands to produce $[MoOCl_3(ligand)_2]$ to dimeric and possibly trimeric oxo-bridged species such as $[Mo_2O_3Cl_4(ligand)_2]$, $[Mo_2O_3Cl_4(ligand)_3]$ and $[Mo_3O_5Cl_5(ligand)_3]$. An attempt is made to relate the steric bulk of the donors to the formation of polynuclear species. For complexes containing nitrogen donors e.p.r. g values are ~1.94, and for sulphur involvement g = 1.967.

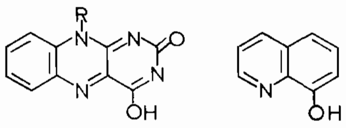

(RibH) (QH)

Figure 1.

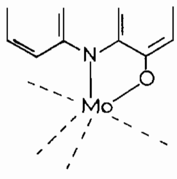


Figure 2.

Introduction

The structures and reactions of complexes of molybdenum, especially in the +5 oxidation state, are of considerable current interest because of the identification of this oxidation state in certain molybdenum-containing enzymes such as xanthine oxidase and aldehyde oxidase [2, 3]; in these systems there are two molybdenum atoms and two flavins per enzyme molecule. Attention in particular has been focused on molybdenum(V) complexes containing sulphur donor ligands since the e.p.r. spectra obtained are consistent with the Mo(V) centre being bound to at least one sulphur atom and g values of ~1.97–1.98 being recorded with the enzymes. However, this supposition may not be entirely valid since we have recently demonstrated that a molybdenum(V) complex containing no sulphur donors exhibits an e.p.r. g value of 1.979 [4] (see below).

In oxidation of substrates via molybdenum-containing enzymes evidence from electron-spin relaxation studies [5, 6] suggests that there is a close interaction between molybdenum and flavin adenine dinucleotide. Although there is evidence that the protein fragment of molybdenum flavoenzymes provides a non-aqueous environment [7] many of the model studies have been carried out in aqueous media [8–10]. In a previous study [4] we employed 8-hydroxyquinoline (QH) as a model to investigate the interaction of molybdenum(V) with this type of group. 8-Hydroxyquinoline is useful because it has a structural similarity with the enol form of the isoalloxazine nucleus of reduced riboflavin (RibH) [11, 12], Fig. 1. It is believed that flavin interacts with molybdenum via coordination, Fig. 2, and if this is so then 8-hydroxyquinoline is a useful, simple analogue. We found [4] that $MoOCl_3(THF)_2$ reacts with QH to form $[MoOCl_3(QH)_2]$, which contains neutral monodentate ligands, $[MoOCl(Q)_2]$ containing anionic bidentate ligands, and the dimeric $[Mo_2O_3(Q)_4]$ containing anionic bidentate ligands and both terminal and bridging oxo donors. In dichloromethane $[MoOCl_3(QH)_2]$ dissolved to give three species and e.p.r. measurements identify these as unchanged $[MoOCl_3(QH)_2]$, $[MoOCl(Q)_2]$ and a third species characterized by a g value of 1.979. No

TABLE I. Analytical Data for Complexes of Oxomolybdenum(V).

Compound	Colour	% C[a]	% H[a]	% N[a]	% Cl[a]	% Mo[a]
$[QSH_2][MoOCl_4(QSH)]$	Dark green	36.4	2.3	(5.1)	24.6	
		(37.5)	(2.4)	(4.9)	(24.6)	
$[MoOCl_3(IQ)_2]$	Brown	45.3	3.0	5.8	19.7	
		(45.4)	(3.0)	(5.9)	(21.3)	
$[MoOCl_3(2,2'\text{-}BQ)]$	Ochre	45.8	2.5	5.9	21.1	
		(45.6)	(2.5)	(5.9)	(22.4)	
$[MoOCl_2(8\text{-}QDH)_2(8\text{-}QD)]$	Dark green	54.4	4.1	7.0	10.7	
		(54.5)	(4.1)	(6.4)	(10.8)	
$[Mo_2O_3Cl_4(3\text{-}MIQ)_2]\cdot 1/2THF$	Purple	37.3	3.3	4.3	20.7	27.6
		(37.5)	(3.1)	(4.0)	(20.1)	(27.3)
$[Mo_2O_3Cl_4(5,6\text{-}BQ)_3]$	Dark brown	51.9	3.0	4.8		21.2
		(50.9)	(2.9)	(4.6)		(20.8)
$[Mo_2O_3Cl_4(6\text{-}MQ)_3]\cdot 3/4CH_2Cl_2$	Red brown	43.2	3.7	4.6	22.2	21.6
		(42.2)	(3.3)	(4.8)	(21.9)	(21.9)
$[Mo_3O_5Cl_5(7\text{-}MQ)_3]$	Light brown	36.8	3.3	4.3	17.7	
		(36.9)	(3.3)	(4.3)	(18.2)	

[a] Calcd. (Fd.)

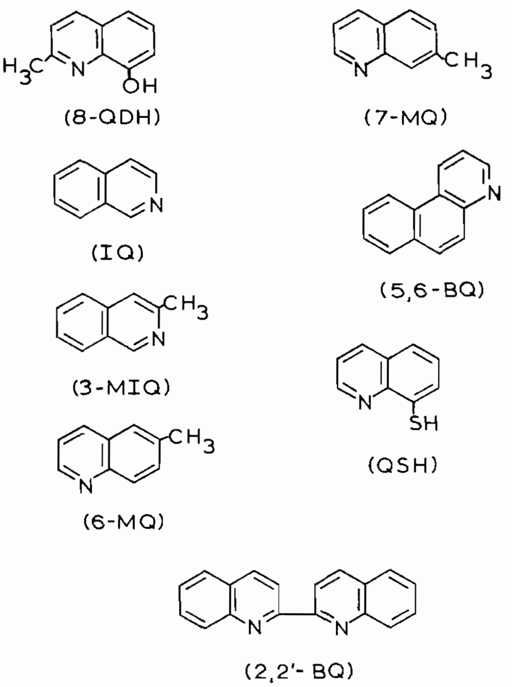


Figure 3.

g values of this magnitude has previously been obtained for molybdenum(V) complexes which do not contain sulphur donors, and the significance of e.p.r. measurements as an indication of the nature of molybdenum coordination in flavoenzymes must be questioned.

In this paper we wish to report further studies we have made on molybdenum(V) complexes of substituted hydroxyquinolines and quinolines. The ligands employed were 8-hydroxyquinolidine (8-QDH), isoquinoline (IQ), 3-methylisoquinoline (3-MIQ), 6-methylquinoline (6-MQ), 7-methylquinoline (7-MQ), 5,6-benzoquinoline (5,6-BQ), 8-mercaptoquinoline (QSH), and 2,2'-biquinolyl (2,2'-BQ). For convenience we have drawn these structures in Fig. 3, and it can be seen that this particular selection of ligands may allow some insight into steric factors affecting structure/stoicheiometry of the resulting complexes.

Results and Discussion

The reaction of $MoOCl_3(THF)_2$ with the quinolines in acetonitrile or toluene/dichloromethane in a 1:2 molar ratio under dinitrogen yields various types of complexes, Table I. The infrared spectra of these compounds exhibit strong ν(Mo=O) at 980–930 cm^{-1}, consistent with terminal Mo=O bonds [13], and strong partially resolved ν(Mo–Cl) vibrations at 280–360 cm^{-1}. In addition, in some cases there are two absorptions at 750 and 430 cm^{-1}, assignable to ν(Mo–O–Mo) vibrations [14], Table II. All of the complexes exhibit two broad absorptions in the visible region. For the six-coordinate complexes the band in the 12,000–16,000 cm^{-1} region is assigned to $^2B_2 \rightarrow {}^2E_1$ and the band at ~24,000 cm^{-1} is assigned to $^2B_2 \rightarrow {}^2B_1$ transitions for O_h symmetry. The room temperature magnetic moments are in the range 1.2–1.6 μ_B consistent with d^1 species, Table III.

From the reaction of $MoOCl_3(THF)_2$ with 8-mercaptoquinoline in acetonitrile only black tar-like substances were obtained, even after a number of attempts to vary the preparative conditions. However, using 8-mercaptoquinoline hydrochloride (QSH_2Cl)

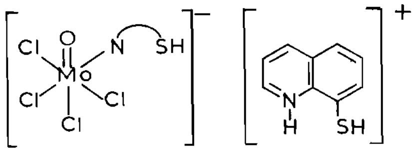
TABLE II. Infrared Data of Oxomolybdenum(V) Complexes.

Compound	ν(Mo=O) cm^{-1}	ν(Mo–Cl) cm^{-1}	ν(Mo–O–Mo) cm^{-1}	(Mo–O–Mo) cm^{-1}
$[QSH_2][MoOCl_4(QSH)]$	950	335, 330, 315		
$[MoOCl_3(IQ)_2]$	950	345, 340, 300		
$[MoOCl_3(2,2'\text{-}BQ)]$	950	343, 310		
$[MoOCl_2(8\text{-}QDH)_2(8\text{-}QD)]$	940	330, 340		
$[Mo_2O_3Cl_4(3\text{-}MIQ)_2]\cdot 1/2THF$	960	330, 295	740	
$[Mo_2O_3Cl_4(5,6\text{-}BQ)_3]$	960, 1015	345, 320, 297	750	430
$[Mo_2O_3Cl_4(6\text{-}MQ)_3]\cdot 3/4CH_2Cl_2$	975, 955	350, 315, 310	720	410
$[Mo_3O_5Cl_5(7\text{-}MQ)_3]$	980, 970	350, 340	720	415

TABLE III. Magnetic Moment, U.V. Reflectance and E.p.r. Data for the Oxomolybdenum(V) Complexes.

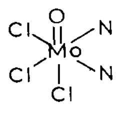
Compound	μ_{eff} B.M. (Room temperature)	U.V. Reflectance $E_{max} \times 10^3$ cm^{-1}	g	A_{iso} (^{95}Mo)G or A_{iso} (^{97}Mo)G
$[QSH_2][MoOCl_4(QSH)]$	1.45		1.967	42
$[MoOCl_3(IQ)_2$	1.21	13.3, 20.4	1.946	50.
$[MoOCl_3(2,2'\text{-}BQ)]$	1.37	13.2, 22.2	1.945	50
$[MoOCl_2(8\text{-}QDH)_2(8\text{-}QD)]$		13.9, 24.1	1.948	48
$[Mo_2O_3Cl_4(3\text{-}MIQ)_2]\cdot 1/2THF$	1.32	12.7, 20.6	1.944	
$[Mo_2O_3Cl_4(5,6\text{-}BQ)_3]$		13.3, 20.6	1.949	
$[Mo_2O_3Cl_4(6\text{-}MQ)_3]\cdot 3/4CH_2Cl_2$	1.57	12.8, 21.3	1.943	
$[Mo_3O_5Cl_5(7\text{-}MQ)_3]$	1.46	12.6, 21.7	1.943	

we were able to isolate dark green crystals of formulation $MoOCl_4(QSH)(QSH_2)$. The infrared spectrum of this complex exhibits a band at 3340 cm^{-1}, which in QSH_2Cl is also present, and is assigned to $\nu(\overset{+}{N}\text{–}H)$ and there is also a band assignable to ν(S–H) at 2720 cm^{-1} both in the complex and in QSH_2Cl. The complex has only slight solubility in most organic solvents but is sufficiently soluble in dry nitromethane to obtain a conductance value (Λ_M = 38 ohm^{-1} cm^2 M^{-1}), which is in the range expected for a 1:1 electrolyte in this solvent [15]. The complex is thus probably $[QSH_2][MoOCl_4(QSH)]$, implying that the anion contains a neutral QSH ligand which is coordinated *via* the nitrogen and is not chelated by N,S donors. The e.p.r. spectrum of this complex in the solid state indicates that only one type of Mo is present, there being one main line due to the isotope ^{96}Mo having nuclear spin I = 0 and hyperfine structure of six lines due to interaction of the unpaired electron with isotopes ^{95}Mo, ^{97}Mo having I = 5/2, g = 1.967, A_{iso} = 42G, Fig. 3. It is probable that this complex has a structure similar to that of (I).



(I)

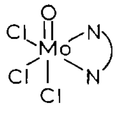
The reaction of $MoOCl_3(THF)_2$ with isoquinoline in acetonitrile gave brown crystals of $MoOCl_3(IQ)$. This complex exhibits μ_{eff} = 1.21 μ_B, and its e.p.r. spectrum in dichloromethane at room temperature exhibits a single broad line, g = 1.946 and A = 50G. Its infrared spectrum exhibits ν(Mo=O) at 950 cm^{-1} and three absorptions assignable to ν(Mo–Cl) at 356, 340 and 300 cm^{-1}, suggesting that the structure is one which has two *cis* chlorines (356, 340 cm^{-1}) and one *trans* to oxygen (300 cm^{-1}) [16]. We thus suggest that this compound has the *fac* structure (II).



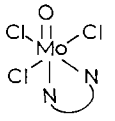
(II)

Reaction of $MoOCl_3(THF)_2$ with 2,2'-biquinolyl in a 1:1 ratio in acetonitrile yields ochre crystals of $MoOCl_3(2,2'\text{-}BQ)$. The infrared spectrum contains ν(Mo=O) at 950 cm^{-1} and there are two low-energy absorptions at 343 and 310 cm^{-1}. There are two possible structures, (III) and (IV) and we think that

(IV) is more likely since there is no ν(Mo–Cl) $\geqslant$ 300 cm^{-1} as there are in a number of other complexes in this series which probably indicate chlorine *trans* to Mo=O. The e.p.r. spectrum of this complex at room temperature in dichloromethane consists of a single broad absorption line g = 1.945, A_{iso} = 50G.

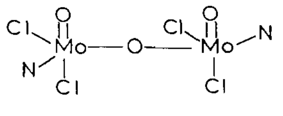


(III)



(IV)

We have isolated complexes of the ligands 3-MIQ, 6-MQ and 7-MQ and it is notable that in each case polynuclear species are obtained. The 3-methylisoquinoline ligand is probably the most sterically hindered and it forms a complex [$Mo_2O_3Cl_4$(3-MIQ)$_2$]·1/2THF. In this compound the $\nu(COC)_{asym}$ and the $\nu(COC)_{sym}$ of the tetrahydrofuran are only very slightly shifted from the values for free THF (1078 and 909 cm^{-1}) indicating that the THF is only present in the lattice since coordination shifts these frequencies to lower energy by ~60 cm^{-1} [17]. No evidence is found for differing molybdenum centres; for example, only one e.p.r. signal is observed g = 1.944 and only one ν(Mo=O) at 960 cm^{-1} appears in the infrared spectrum. The Mo–O–Mo bridge is characterised by the appearance of a band at 740 cm^{-1}. In the low energy region two absorptions at 330 cm^{-1} and 295 cm^{-1} probably indicate that there is one chlorine *trans* to terminal oxygen in each molybdenum centre. The only reasonable interpretation of these results is that the complex has structure

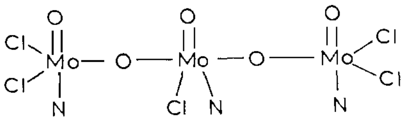


(V)

(V). It is somewhat surprising that such a pentacoordinate structure does not lead to the ν(Mo–O) appearing at much higher frequencies; for example in $[MoOCl_4]^-$ ν(Mo=O) occurs at 1015 cm^{-1} [18]. However, it is not known just what effect dimerisation has on the energy of this band in pentacoordinate complexes. Since the reaction conditions for the preparation of this complex are identical to those mentioned previously the non-formation of [$MoOCl_3$(3-MIQ)$_2$] deserves some comment. It seems reasonable to speculate that such a six-coordinate complex does not form on steric grounds; indeed it is likely that each molybdenum in [$Mo_2O_3Cl_4$(3-MIQ)$_2$] is pseudo-hexacoordinate with the sixth coordination position in each case being blocked by an organic group. The rigorously oxygen-free conditions preclude abstraction of oxygen from air and the bridging oxygen in the dimer is probably the result of oxygen abstraction from THF [19, 20] in a reaction which probably has a similar stoichiometry to:

$$2MoOCl_3(THF)_2 + 2L \longrightarrow Mo_2O_3Cl_2L_2 + Cl(CH_2)_4Cl + THF$$

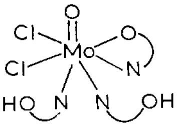
The reaction of $MoOCl_3(THF)_2$ with 6-MQ in a 50/50 dichloromethane/toluene mixture yields red-brown crystals of [$Mo_2O_3Cl_4$(6-MQ)$_3$]·3/4CH_2Cl_2, a stoicheiometry which differs from the last complex in having one more ligand. That this stoicheiometry would lead to an unsymmetrical dimer is confirmed by the fact that two ν(Mo=O) bands are seen at 975 and 955 cm^{-1}, and the bridging Mo–O–Mo group is once again characterised by the appearance of bands at 720, 410 cm^{-1}; there is also an extremely broad e.p.r. signal g = 1.943. In this case there can be no question of the methyl group having any steric interaction in the process of complex formation. Moreover it is interesting to observe that the isoquinoline ligand, which contains a very unrestricted nitrogen donor, yields a "normal" [$MoOCl_3(IQ)_2$] species, whereas it is a reasonable assumption that in the case of 6-methylquinoline the fused ring adjacent to the nitrogen donor does exert some steric control over resulting stoicheiometry. However, the electronic effect of the methyl group might play some role because one observes that the reaction of the 7-methylquinoline with $MoOCl_3(THF)_2$ in acetonitrile yields light brown crystals of $Mo_3O_5Cl_5$(7-MQ)$_3$, the infrared spectrum of which shows ν(Mo=O) at 980, 970(sh) cm^{-1}, Mo–O–Mo at 720, 415 cm^{-1} and terminal (presumably *cis* to Mo=O) ν(Mo–Cl) at 350, 340 cm^{-1}. The complex is much too insoluble for conductance measurements which might shed light on the possibility of a complex cation/anion formulation. If the compound is, in fact, a trimer then it is likely that structure (VI) bears some resemblances to reality, and does fit the available evidence well, though other structures are possible.



(VI)

The importance of steric interactions of neighbouring fused rings is further seen by the isolation of [$MoOCl_3(IQ_2)$], on the one hand, but by the isolation of $Mo_2O_3Cl_4$(5,6-BQ)$_3$ in an identical reaction on the other hand.

We have also observed that placing a methyl group at the 2-position in 8-hydroxyquinoline endows the ligand, 8-hydroxyquinolidine (8-QDH), with quite different donor properties from 8-hydroxyquinoline. By the reaction of 8-QDH with $MoOCl_3(THF)_2$ in acetonitrile we have been able to isolate only one complex, the elemental analyses and physical properties of which suggest it to be $MoOCl_2(8\text{-}QDH)_2(8\text{-}QD)$. This complex clearly contains molybdenum(V), exhibiting $\mu_{eff} = 1.45\mu_B$ at room temperature and a single broad e.p.r. absorption g = 1.948, A_{iso} = 48G in dichloromethane at room temperature. Thus, expulsion of HCl accompanies complex formation and one ligand is present as the anion 8-QD. Terminal Mo=O is present, evidenced by a strong infrared band at 940 cm^{-1}, and the two ν(Mo–Cl) absorptions at 340 and 330 cm^{-1} may be tentatively interpreted as arising from mutually *cis* chlorines which are also *cis* to Mo=O, indicating a structure such as (VII).



(VII)

In conclusion we would like to emphasise that the structures of the quinoline adducts of oxomolybdenum(V) are clearly very much influenced by steric factors on the ligand. In general g values for these nitrogen-donor ligand complexes are ~1.94 and where sulphur is involved we observe g = 1.967.

Experimental

Reagents

Tetrahydrofuran (THF) was dried by refluxing over sodium wire and finally distilling from sodium benzophenone ketyl under N_2 prior to use. Diethylether was dried over sodium wire. Acetonitrile was dried by distilling from phosphorus pentoxide (P_2O_5). Carbon tetrachloride (CCl_4) was dried by distilling off the first 10% of the solvent which contained the CCl_4–H_2O azeotropic mixture. The remaining dry CCl_4 was used. Other solvents and reagents were of the best grade commercially available and were used without further purification other than drying over 4-A molecular sieves.

Sample Handling and Reaction Techniques

All reactions and manipulations were carried out using a N_2/vacuum system Schlenk apparatus and a dry N_2-filled glove-box. A slight positive N_2 pressure was maintained in the glove-box at all times. All reaction apparatus was predried in an oven and assembled while hot. The apparatus was then evacuated for an additional 5 minutes and finally refilled with dry N_2. All sample transferring was done in the N_2 filled glove-box and samples were packed and sealed in dry N_2 filled glass tubes and used for analyses and other physical measurements.

Physical Measurements

Infrared spectra

Infrared spectra were obtained in Nujol and hexachlorobutadiene mulls, in the range 4000–200 cm^{-1} on the Perkin Elmer 621 spectrophotometer using caesium iodide plates.

Electronic spectra

Reflectance spectra were measured on a Beckman Acta M4 spectrophotometer using magnesium oxide as dilutant and reference. Intensities are arbitrary.

Conductivities

Conductivities were measured in nitromethane (specific conductance 1 × 10^{-5} ohm^{-1}) solutions at 20 °C on a Cambridge Instruments Ltd conductivity bridge using a glass cell fitted with platinised electrodes previously calibrated with standard potassium chloride solution as described [21].

Electron paramagnetic resonance spectra

The electron paramagnetic resonance spectra (epr) were run in dichloromethane solutions at room temperature and −150 °C on a Varian E9 spectrometer in dual cavity mode and referenced to a strongpitch (g = 2.0028).

Magnetic measurements

Magnetic susceptibilities were measured on a Newport Instrument Single Temperature Gouy Balance system with a type A magnet and employing a Mettler H51 microbalance. Mercury tetrathiocyanatocobaltate(II), $\chi_M = 16.44 \times 10^{-6}$ c.g.s., was used as a calibrant. The effective magnetic moment μ_{eff} is obtained from $\mu_{eff} = 2.84\,(\chi_M^{corr}\,T)^{1/2}$. χ_M^{corr} is the magnetic susceptibility per mol, corrected for diamagnetism by the use of Pascal's Constants, and T is the absolute temperature (K).

Microanalyses

Carbon, nitrogen, halogen and molybdenum analyses were performed by the Microanalytical service at UMIST.

Preparation of Oxotrichlorobis(tetrahydrofuran)-molybdenum(V)

Oxide-free molybdenum pentachloride (20 g) was added to a dry dinitrogen filled 500 cm^3 3-necked flask fitted with a pressure equalizing dropping funnel, N_2 inlet system and a condenser. Dry CCl_4 (150 cm^3) was added and the $MoCl_5$ dissolved to give a red solution. Freshly distilled THF (50 cm^3) was added using the dropping funnel and within a short time a highly exothermic reaction took place and the solution turned green. As the solution cooled, green crystals formed and these were collected by vacuum filtration using a Schlenk apparatus, washed with

10 cm^3 of CCl_4 and 10 cm^3 of pentane and were dried *in vacuo*. The Schlenk tube containing the $MoOCl_3(THF)_2$ was placed in a N_2 filled glove-box and the $MoOCl_3(THF)_2$ was packed into dry N_2 filled glass ampoules so that each ampoule contained 1 to 2 g of $MoOCl_3(THF)_2$. The ampoules were then sealed off under N_2 and stored until needed. The $MoOCl_3(THF)_2$ keeps for as long as 9 months without any noticeable deterioration (yield 80%). This complex was characterised by infrared, epr (g_{iso} = 1.940) and microanalysis. The compound is very unstable to moisture and rapidly turns to a dark green then a blue tar in the presence of traces of moisture. The compound dissolves to give a green solution in absolutely dry solvents such as EtOH, toluene, benzene, CH_2Cl_2 and $CHCl_3$.

Preparation of Molybdenum(V) Complexes with Quinolines

All the molybdenum(V) complexes were made employing the same techniques as for $MoOCl_3(THF)_2$ except where otherwise stated. The following description of the preparation of oxotrichlorobis(8-hydroxyquinoline)molybdenum(V), $MoOCl_3(8\text{-}QLH)_2$ is typical.

Oxotrichlorobis(tetrahydrofuran)molybdenum(V), (1.92 g, 5 mmol) was added to a dry dinitrogen filled 250 cm^3 3-necked flask cooled in an ice bath fitted with a pressure equalizing dropping funnel, N_2 inlet system. Dry CH_3CN (100 cm^3) was added and $MoOCl_3(THF)_2$ dissolved to give brown solution of $MoOCl_3(MeCN)_2$. Dry 8-hydroxyquinoline (1.54 g, 0.01 mol) dissolved in acetonitrile (30 cm^3) under N_2 atmosphere was added using the dropping funnel and stirred for 0.5 hr. The green crystals were collected by vacuum filtration using a Schlenk apparatus, washed with acetonitrile (2 × 5 cm^3) and sodium dried diethylether (2 × 5 cm^3) and were dried *in vacuo*. The Schlenk tube containing the $MoOCl_3(8\text{-}QLH)_2$ was placed in a N_2 filled glove-box and the $MoOCl_3(8\text{-}QLH)_2$ was packed into dry N_2 filled glass ampoules. The ampoules were then sealed off under N_2 and stored (yield 85%). This complex was characterised by infrared, epr, mocroanalysis, electronic spectra and magnetic moment.

Preparation of $[QSH_2]$ $[MoOCl_4(QSH)]$

Oxotrichlorobis(tetrahydrofuran)molybdenum(V), (0.61 g) was added to a dry dinitrogen filled 250 cm^3 3-necked flask fitted with a pressure equalising dropping funnel, N_2 inlet system and a condensor. Dry acetonitrile/n-butanol (50:50 mixture, 30 cm^3) was added and $MoOCl_3(THF)_3$ dissolved to give a brown solution. Dry 8-mercaptoquinolinehydrochloride (0.66 g) dissolved in acetonitrile/n-butanol (50:50 mixture, 30 cm^3) under dinitrogen atmosphere was added using the dropping funnel and refluxed for 4 hr. As the solution cooled, dark green crystals were collected by vacuum filtration using a Schlenk apparatus, washed with acetonitrile/n-butanol (2 × 5 cm^3) and diethylether (2 × 5 cm^3) and were dried *in vacuo*. This experiment was carried out by a similar route to the other complexes (yield ~85%).

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