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Coordination Chemistry of Molybdenum. Part III.* EPR Spectra of Molybdenum(V) 8-Hydroxyquinoline Complexes and their Relevance to the Nature of Molybdenum Coordination in Flavoenzymes

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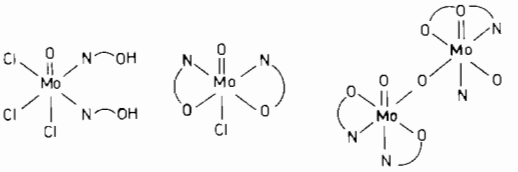
Although there is evidence that the protein fragment of molybdenum flavoenzymes provides a non-aqueous environment[1] many model studies on flavoenzymes have been in aqueous media.[2] EPR has been the most widely used investigative spectroscopic technique both on the flavoenzymes and model systems; and on the basis of g values of ~ 1.98 it has been assumed that sulphur ligands are involved in the active site.[3] We are currently investigating model xanthine oxidase systems, with particular attention to 8-hydroxyquinoline as a ligand; the structural similarity of 8-hydroxyquinoline to the enol form of the isoalloxazine nucleus has been previously noted.[4] We wish to report EPR g values for these complexes one of which suggests that sulphur donors are not necessarily involved in molybdenum flavoenzymes.

By reacting $MoOCl_3(CH_3CN)_2$ with 8-hydroxyquinoline (LH) in acetonitrile at room temperature in anaerobic conditions a light green complex, $MoOCl_3(LH)_2$, (I),[5] $\mu_{eff} = 1.48$ B.M., is formed. It is unusual for 8-hydroxyquinoline to bond as a neutral donor, but IR absorptions at 3325, 3220 cm^{-1} confirms the presence of unionised –OH groups; there is also a single strong absorption at 943 cm^{-1} assigned to ν(Mo=O). By reacting $MoOCl_3(THF)_2$, LH, and LiOEt in ethanol the expected deprotonation occurs and the known $MoOCl(L)_2$,[6] (II), results. When either (I) or (II) is refluxed with Et_3N in ethanol under aerobic conditions the dimeric oxo-bridged $Mo_2O_3L_4$, (III),[7] is formed; this is a novel route to this complex.



(I) (II) (III)

We have studied the EPR of complexes (I) and (II) in the solid state and in solution in dichloromethane and N,N-dimethylformamide (Table).

TABLE. EPR Spectra.

Compound	State	g_{av}[a]			
		X	A	B	Y
$MoOCl_3(LH)_2$	Solid	1.951			
	CH_2Cl_2	1.951 (48G)		1.937 (51G)	1.979
	DMF	1.950 (46G)			
$MoOCl(L)_2$	Solid		1.941		
	CH_2Cl_2		1.953 (43G)	1.937 (46G)	
	DMF		1.953 (43G)	1.939 (46G)	

[a] Values in brackets are a, the isotropic hyperfine splitting constants.

Complex (I) in the solid state exhibits a broad absorption $g = 1.951$ and no hyperfine splitting is observed, and in DMF one species is obtained – the spectrum consists of one main line (^{96}Mo, I = 0), $g = 1.950$, and hyperfine splitting of six lines (^{95}Mo, ^{97}Mo, I = 5/2), a spectrum typical of monomeric Mo(V). However, in CH_2Cl_2 there is evidence for three separate species (X, B, Y). Complex (I) dissolves to give X with structure unchanged, to give the deprotonated species B, and to give a third species, Y, characterised by $g = 1.979$. No g value of this magnitude has hitherto been observed in molybdenum complexes which do not contain sulphur donors, and the acceptance of molybdenum–sulphur coordination in flavoenzymes[3] has stemmed largely from the high EPR g values of the enzymes. While we do not know the structure of species Y it is quite clear that no molybdenum–sulphur coordination is possible, and we thus suggest that deductions about the nature of

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the active site in flavoenzymes based on g values are unwise.

Our EPR results for complex (II) indicate that there are two isomers present in solution (species A and B) in CH_2Cl_2 and DMF, and the broadness of the solid state absorption and the g value suggests that these two isomers are also present in the solid state.

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5 All complexes gave satisfactory analyses. Structures (I), (II), (III) appear to us to fit our available spectroscopic characterisation data; but other isomeric forms are possible.

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