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Oxomolybdenum(V) and Oxotungsten(V) Complexes of a Tritertiary Arsine

W. LEVASON

Department of Chemistry, The University of Southampton S09 5NH, U.K.

C. A. McAULIFFE and F. P. McCULLOUGH

The University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

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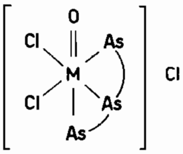
We have recently reported [1–3] a series of oxomolybdenum(V) and oxotungsten(V) complexes [$MOCl_3(L–L)$] (M = Mo, W), of bidentate phosphorus and arsenic donor ligands (L–L). As an extension of this work we have examined the corresponding complexes of the triarsine bis(3-dimethylarsino-propyl)phenylarsine; $PhAs(CH_2CH_2CH_2AsMe_2)_2$ (tasp).

The reaction of [$WOCl_3(THF)_2$] with tasp in a 1:1 ratio in toluene–dichloromethane produced yellow-green $WOCl_3$(tasp). The complex is very moisture sensitive and poorly soluble in non-polar solvents, but in rigorously dry nitromethane (10^{-3} *M*) it is a 1:1 electrolyte. The spectroscopic and magnetic properties (Table) are consistent with the presence of a W=O group, but provide no further information about the structure. However the fluid solution ESR spectrum shows only one species to be present (g_{iso} = 1.850) with superhyperfine coupling appearing as a 1:2:3:4:3:2:1 septet [A(^{75}As) ≅ 30 G] showing the unpaired electron is coupled to two equivalent arsenics (^{75}As I = 3/2 100%). The spectrum is shown as a double derivative in Fig. 1. We have previously observed [3] that coupling of the electron to P or As *trans* to the W=O bond is much less marked than to similar donors *cis* to the double bond, and that often the coupling to the *trans* ligand is not observed. On the basis of the ESR spectrum and conductivity data the complex is formulated [$WOCl_2$(tasp)]Cl (I) in solution, and probably has the same structure in the solid state.



I

(A second isomer with the central arsenic donor of tasp *trans* to W=O is also possible. The data is consistent with a facial arrangement of the arsenic donors, but does not distinguish the conformation of the tridentate).

The $MoOCl_3$(tasp) complex was prepared in an analogous manner from [$MoOCl_3(THF)_2$]. However the IR spectrum exhibited two ν(Mo=O) vibrations, and the conductivity in 10^{-3} *M* nitromethane (Table) was intermediate between the values expected for a non-electrolyte and a 1:1 electrolyte. The fluid solution ESR spectrum (Fig. 2) confirms that two molybdenum(V) species are present in approximately equal amounts. One species is similar to [$WOCl_2$(tasp)]Cl having g_{iso} = 1.980 with a septet superhyperfine coupling pattern, A_{iso} (^{75}As) = 22 G. The second species has g_{iso} = 1.933 and shows a 1:1:1:1 quartet, A_{iso} (^{75}As) = 9.5 G, due to coupling to a single arsenic *cis* to the Mo=O unit. The lower g_{iso} value is consistent with replacement of one arsenic by

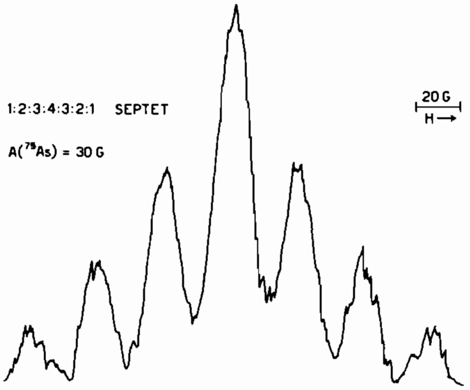


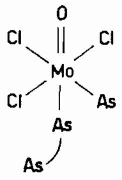
Figure 1. Double derivative ESR spectrum of $WOCl_3$(tasp) in CH_2Cl_2 at 25 °C.

TABLE. Analytical and Spectroscopic Data.

	Colour	C%^{a}	M%^{a}	Cl%^{a}	ν(M=O) cm^{-1b}	ν(M–Cl) cm^{-1b}	E_{max} (kK)^c	Λ_M ohm^{-1} cm^2 M^{-1d}	μ_{eff} (B.M.)
[$WOCl_3$(tasp)]	Yellow–Green	22.9 (22.9)	3.4 (3.8)	15.0 (14.2)	960	330, 305	22.7, 14.1br, 12.3	50	1.34
[$MoOCl_3$(tasp)]	Drab–Green	29.3 (28.9)	4.3 (4.4)	15.5 (16.0)	975, 958	330, 310, 290	23.8, 16.3, 13.7	30	1.60

^{a}Found (calc). ^{b}Nujol mulls. ^{c}Diffuse reflectance. $^d10^{-3}$ *M* nitromethane 1:1 electrolytes have values of ~50–90 in this solvent [5].

chlorine, and structure (II) is tentatively proposed for this species. Attempts to confirm the presence of an uncoordinated $-AsMe_2$ by ^1H NMR spectroscopy were frustrated by the low solubility and rapid decomposition of this complex in suitable solvents. The observed conductivity is consistent with the presence of approximately equal amounts of the 1:1 electrolyte (I) and the non-electrolyte (II). Attempts to isolate the $[MoOCl_2(tasp)]^+$ cation with BPh_4^- or ClO_4^- anions were not successful.



II

Speculation upon the causes of the different behaviour of molybdenum and tungsten towards tasp seems unprofitable at present, but it is apparent that isomers I and II of the molybdenum complex must differ little in stability.

Experimental

The complexes were prepared by reaction of the appropriate $[MOCl_3(THF)_2]$ with tasp [4] in an analogous manner to that of the bidentates previously described [1–3]. Physical measurements were made as described [1].

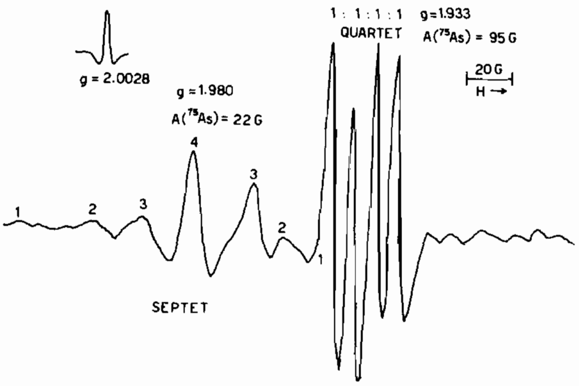


Figure 2. Double derivative ESR spectrum of $MoOCl_3$(tasp) in CH_2Cl_2 at 25 °C.

Acknowledgement

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