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Preliminary communication

Fast atom bombardment mass spectra of anionic peroxo-molybdenum and -tungsten complexes

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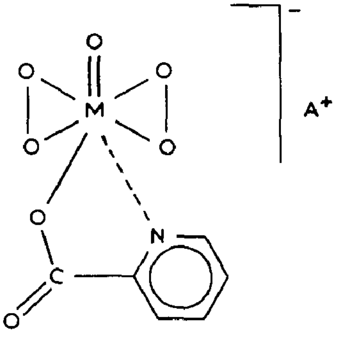
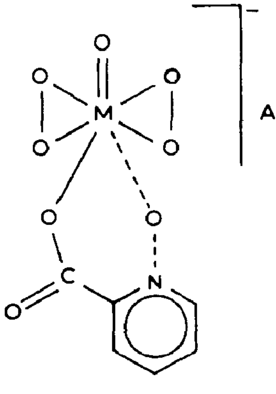
Abstract

FAB negative ion mass spectra of some anionic peroxo complexes are described, and some differences between tungsten(VI) and molybdenum(VI) compounds are noted.

Anionic peroxo-molybdenum(VI) and -tungsten(VI) complexes are useful reagents for alcohol oxidations. The synthesis, the structure, and the solution properties of $[MO(O_2)_2PIC]^-$ (**1**) and $[MO(O_2)_2PICO]^-$ (**2**) have been described previously [1].



(**1a**, M = Mo ;
1b, M = W)



(**2a**, M = Mo ;
2b, M = W)

($A^+ = H_3O^+$, Me_4N^+, Bu_4N^+)

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Table 1

FAB negative ion mass spectra of peroxo-molybdenum and -tungsten derivatives [a]

	1a, M = Me			**1b**, M = W		
	m/z	FAB (%)	MIKE (%)	*m/z*	FAB (%)	MIKE (%)
$[MO(O_2)_2PIC]^-$	294	100		384	50	
$[MO(O_2)_2PIC\text{-}O]^-$	278	15	95	368	30	100
$[MO(O_2)_2PIC\text{-}2O]^-$	262	50	60	352	90	30
$[MO(O_2)_2PIC\text{-}CO_2]^-$	250	15	10	340	10	35
$[MO(O_2)_2PIC\text{-}3O]^-$	246	10	40	336	20	-
$[MO(O_2)_2PIC\text{-}C_4H_4]^-$	242	5	20	332	15	55
$[MO(O_2)_2PIC\text{-}Py]^-$	216	60	100	306	100	50
$[MO(O_2)_2PIC\text{-}PIC]^-$	172	30	-	262	65	20
	2a, M = Mo			**2b**, M = W		
	m/z	FAB (%)	MIKE (%)	*m/z*	FAB (%)	MIKE (%)
$[MO(O_2)_2PICO]^-$	310	75		400	100	
$[MO(O_2)_2PICO\text{-}O]^-$	294	50	50	384	30	-
$[MO(O_2)_2PICO\text{-}2O]^-$	278	25	20	368	10	45
$[MO(O_2)_2PICO\text{-}CO_2]^-$	266	45	100	356	25	100
$[MO(O_2)_2PICO\text{-}3O]^-$	262	35	50	352	20	-
$[MO(O_2)_2PICO\text{-}C_4H_4]^-$	258	30	-	348	40	55
$[MO(O_2)_2PICO\text{-}PyO]^-$	216	100	70	306	75	10
$[MO(O_2)_2PICO\text{-}PICO]^-$	172	30	-	262	50	45

[a] FAB spectra were obtained with a VG ZAB2F spectrometer, with 8 keV Xe atom bombardment of glycerol solutions of **1** or **2**. Relative intensities refer to ions with ^{92}Mo and ^{182}W. Py an PyO denote pyridine and pyridine *N*-oxide, respectively.

These complexes exhibit a slightly distorted bipyramidal arrangement, with the four peroxo oxygens and the carboxylato oxygen in the equatorial plane, and the oxo oxygen occupying one of the two apical positions, and the other apical coordination site may be occupied either by the pyridine nitrogen or by the *N*-oxide oxygen [1]. Compounds of type **1** and **2**, in particular those with $A^+ = Bu_4N^+$, are soluble in aprotic solvents, and readily oxidize primary and secondary alcohols to the corresponding carbonyl compounds [1a,2].

Fast atom bombardment (FAB) mass spectrometry is a relatively new technique for obtaining mass spectral data (of both negative and positive ions) from polar and thermally lable molecules [3a], and has been successfully employed in the organometallic field [3b,c,d]. We report here observations on the mass spectra of **1** and **2**, in glycerol matrix, obtained by this technique. The electron impact mass spectra, of these complexes did not show either molecular ions or fragment ions which could be easily related to the original structures; this can be ascribed to extensive pyrolysis during the sample evaporation. To our knowledge the study described here is the first mass spectrometric examination of metalloperoxo compounds.

The results are summarized in Table 1. A molecular ion is observed in high abundance for all the compounds, and there was no evidence for replacement of the pyridine or pyridine *N*-oxide carboxylato ligands by glycerol. The molecular ions undergo fragmentation with extensive deoxygenation, as expected for such peroxo compounds; this deoxygenation is more pronounced for the molybdenum than for the tungsten complexes. The loss of oxygen, represents the 60% of the total ion current for **1a** compared with 45% for **1b** and 45% for **2a**, compared with 20% for **2b**, as shown by the MIKE spectra [4].

The more significant decomposition, however, is represented by the loss of pyridine or pyridine *N*-oxide carboxylato ligands (PIC or PICO) with formation of an oxodiperoxo anion of the type $[MO_5]^-$ what is observed only in the case of the peroxo tungsten compounds.

These findings can be accounted for in terms of either (i) the greater intrinsic thermodynamic stability of the peroxotungsten complexes than of the molybdenum compounds and (ii) the higher electronic affinity of $[WO_5]^-$ than of $[MoO_5]^-$.

If the effects were due to a low electronic affinity of $[MoO_5]$, however, strongly abundant ions due to PIC^-, $PICO^-$ or related fragments would be expected in the MIKE spectra; their absence rules out this explanation, and so supports the interpretation in terms of the thermodynamic stability of the W derivatives.

Mass spectral data for these organometallics reflect clearly aspects of the known solution behaviour of **1**, **2** and of similar neutral peroxo-molybdenum and -tungsten compounds of the type $MO(O_2)_2HMPT$, H_2O ($M = Mo^{VI}$, W^{VI}; HMPT = hexamethylphosphoric acid triamide) [5], namely the lower affinity of peroxotungsten(VI) species, compared with peroxomolybdenum(VI) species, for the ligands [1d,6] and the ability of the tungsten compounds to exist as oxodiperoxo species also in solution.

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