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Synthesis of $[W_3(TMPO)_5(\mu\text{-}O)_2(O)_3]$ and its Characterisation by Fast Atom Bombardment Mass Spectrometry

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Fast atom bombardement (FAB) mass spectrometry is a relatively new technique which uses a stream of neutral atoms (argon or xenon) to sputter ions from solids or liquids [1]. The utility of the method is in its ability to generate ions from solutions in relatively non-volatile liquid matrices (glycerol, thioglycerol), allowing the recording of spectra (both of negative and positive ions) of polar molecules, ionic complexes, and particularly in the present context, of a high molecular weight organometallic compound, all of which are involatile or thermally labile under 'normal' electron impact source conditions. Perhaps the most complex of organometallic compositions to be studied, which have been hailed as an indicator of the use of this new technique, are vitamin B_{12} and its co-enzyme [2].

Alper has already reported in 1973 the reaction of $W(CO)_6$ with TMPO but only a carbonyl free organometallic compound '$W_3(TMPO)_2$' was postulated [3], this has not subsequently been identified. We wish to report the synthesis of the title compound prepared by the photochemical route described by us [4]. The new trimeric title compound was characterized by FAB mass spectrometry. The mass spectrum of $[W_3(TMPO)_5(O)_5]$ confirms a high molecular weight complex (Fig. 1). High resolution spectra (Fig. 2a) are in accordance with the simulated isotopic pattern distribution (Fig. 2b). From the molecular ion peak (found 1410, calculated 1412) fragmentation occurs first by successive deoxygenation and then by loss of WO_2 groups. The existence of three membered M–N–O metallacycles has recently been documented for Mo and V with hydroxylamine and its N-substituted analogues [5]. In accordance with our spectroscopic data and the reported structure of the dimeric $(Et_2NO)_2VO(\mu\text{-}O)VO(ONEt_2)_2$ [6] we suggest for the title compound a similar 'open chain trimeric' peroxo-like structure with 'side-on' coordinated TMPO ligands.

Experimental

A solution of 3.51 g (10.0 mmol) $W(CO)_6$ and 3.12 g (20 mmol) 2,2,6,6-tetramethylpiperidinyl-1-oxo in n-pentane (500 ml) was irradiated for 7.5 h at 0 °C. During photoreaction the initially white solution turned darker. The yellow precipitate was filtered (G4), washed with n-pentane and dried under vacuum (10^{-2} mm Hg, room temperature, yield >20%, soluble in CH_2Cl_2, non-soluble in n-pentane,

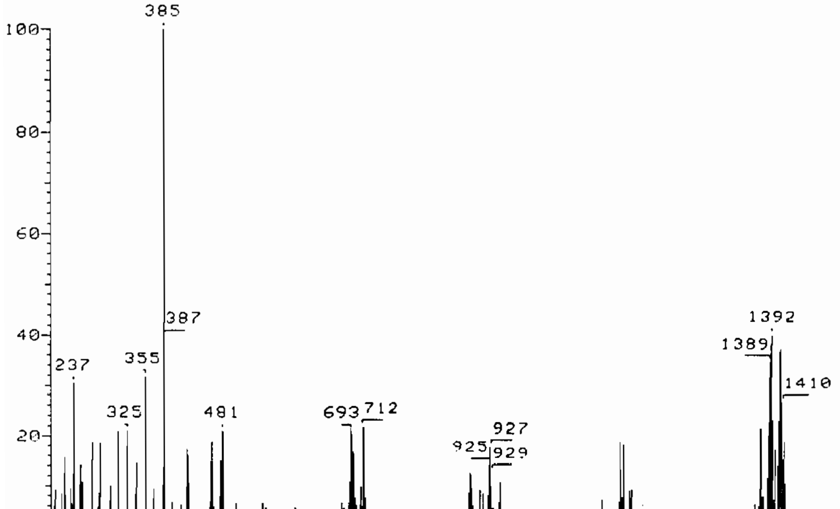

Fig. 1. The mass spectrum of $[W_3(TMPO)_5(O)_5]$ (Neg. FAB, Matrix Tetraethylenglycol, BOE-GOE Finigan 8230).

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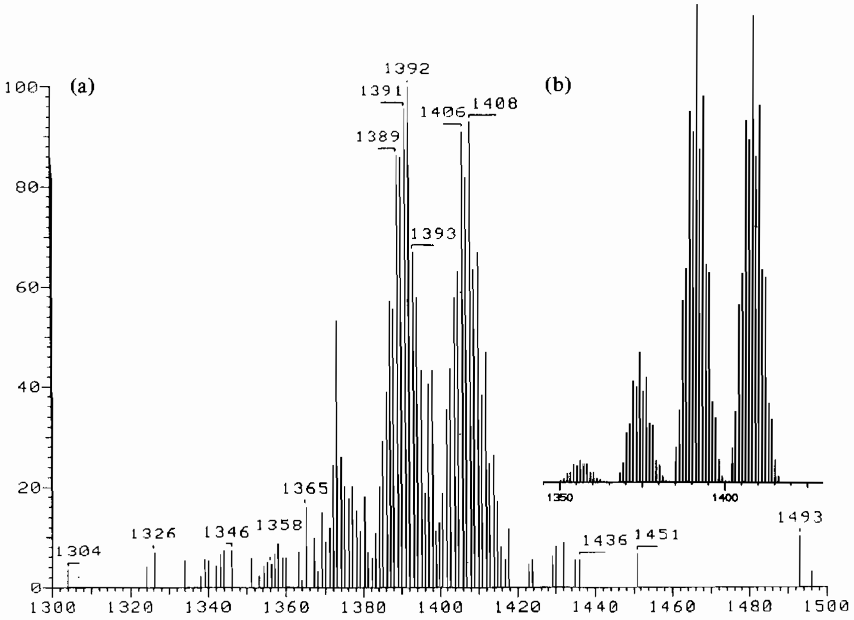

Fig. 2. High resolution spectra (2a) and simulated isotopic pattern distribution (2b) for $[W_3(TMPO)_5(O)_5]$.

benzene, toluene and ether). All manipulations were carried out under dry argon. Solvents were distilled from sodium wire under N_2. Ultraviolet irradiations were performed with a high pressure mercury lamp (Hanau 150 W) in a Schlenk tube equipped with a pressure valve. A minor impurity, probably a tungsten carbonyl compound, was detected by IR spectroscopy (ν_{CO}: 1920, 1860 cm^{-1}, KBr).

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