Dimethylsulphoxide reductase (DMSOR) from the photosynthetic bacterium *Rhodobacter capsulatus* is a periplasmic respiratory oxomolybdenum enzyme which can utilise dimethylsulphoxide, trimethylamine N-oxide and chlorate as electron acceptors [1,2]. The enzyme, with the closely related one from *R. sphaeroides* [3], appears [4] to be unique in containing the molybdenum cofactor as the sole redox centre, and therefore the potential for optical study of the molybdenum centre is large. Preliminary e.p.r. studies [3,5,6] of DMSOR have demonstrated that the enzyme can display at least two different Mo(V) e.p.r. signals. Dithiolene S→Mo(V) charge transfer transitions have been identified [5,6] as contributing to magnetic circular dichroism spectra from DMSOR. However, detailed characterisation of the Mo(V) ion by e.p.r. has not previously been carried out.

A number of Mo(V) e.p.r. signals were generated from DMSOR and are shown in Fig. 1. The close agreement between experimental spectra and computer simulations indicates that each signal corresponds to a single chemical species. The signals shown in (a) and (b) are comparable to those reported previously [3,5,6], though we estimated the e.p.r. parameters (data not shown) considerably more precisely than had been done in the earlier work, and we also studied the effects of buffer ions and of various additives. These two signals are quite like signals [7] from *E. coli* nitrate reductase but, unlike those from that enzyme, are not in pH-dependent equilibrium with one another.

On reduction of DMSOR under specific conditions with Na$_2$S$_2$O$_7$, we observed two new signals (Fig 1c and d) at considerably lower g-values. These are quite unlike the other signals from DMSOR. Both show splitting from interaction of Mo(V) with a single strongly coupled proton. Parameters for the signal of Fig 1c were: $g_{1,2}$, 1.9702, 1.9678, 1.9560; $A(1H)_{1,2,3}$ 1.29, 1.15, 1.27 mT. These parameters for the signal of Fig 1c are similar to the parameters of the Slow signal from xanthine oxidase in the desulpho form and particularly to the Nitrate form of that signal [8]. This is the first instance of an enzyme exhibiting Mo(V) e.p.r. signals typical of more than one oxomolybdenum enzyme family [cf.9] and suggests an unusual degree of flexibility of the molybdenum centre of DMSOR. Comparison with data on model compounds [e.g. 10] makes it clear that either a change of a ligand atom (e.g. from S to O or N) or a significant change of coordination geometry is required to convert the molybdenum centre of DMSOR from the states giving the signals of Figs 1(a) and (b) to those giving the signals of Figs 1c(d) and (d). Since the latter signals were obtained only on reduction with Na$_2$S$_2$O$_7$ and could not be generated, e.g. with MV$^+$ plus NaHSO$_3$, we suggest that such changes in the molybdenum environment in DMSOR are triggered by Na$_2$S$_2$O$_7$ reducing the pteridine of the molybdenum cofactor from a dihydro to the tetrahydro state. Further work is required to test this hypothesis, which, if established, would have an important bearing [cf.4] on understanding the diversity of oxomolybdenum enzymes.

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*Abbreviations used: DMSOR, dimethylsulphoxide.*

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**Fig. 1. Representative Mo(V) e.p.r. Signals from Rhodobacter capsulatus Dimethylsulphoxide Reductase.** Experimental spectra are shown as solid lines and computer simulations (11) are shown dashed. Spectra were generated as follows: for (a), the enzyme was reduced with Na$_2$S$_2$O$_7$ and the excess was removed by anaerobic dialysis, in MES buffer, pH 5.6; (b) was from enzyme, as prepared in Biane buffer, pH 8.2 and (c) and (d) were from enzyme in the same buffer, reduced for relatively short times with a moderate excess of Na$_2$S$_2$O$_7$.

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