A Novel Free-radical-containing Molybdenum(V) Complex

By JOEL SELBIN* and JON SHERRILL

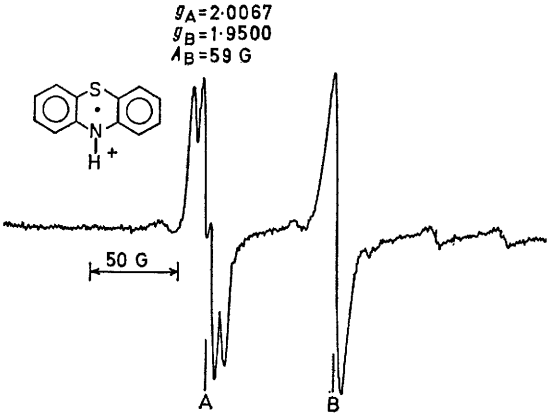
(*Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana* 70803)

Summary The first pure crystalline compound containing a biologically significant molecule as a free radical, apparently complexed to molybdenum(V), phenothiazine cation-radical tetrachloro-oxomolybdate(V), has been synthesized; it exhibits clearly defined e.s.r. signals from both of its unpaired electrons.

THE reaction between $\mathrm{UCl_6^-}$ and phenothiazine (PT), leads to a very stable dark green salt of uranium(IV) containing the phenothiazine cation free radical: $(\mathrm{P\dot{T}})_2\mathrm{UCl_6}$.[1] In view of the importance of phenothiazine and its derivative and of molybdenum in biological systems we investigated the reaction between $\mathrm{Mo^{VI}}$ and PT. The reaction between $\mathrm{MoOCl_4}$ and PT in $\mathrm{CHCl_3}$ yields dark green crystals of $\mathrm{P\dot{T}MoOCl_4}$ (90%), m.p. 190—191 °C (decomp.), $\nu_{\max.}$ (KBr) 978s $\mathrm{cm^{-1}}$ (Mo=O stretch) (*cf.* Mo=O frequencies[2] in several salts of $\mathrm{MoOCl_4^-}$ at *ca.* 1010 $\mathrm{cm^{-1}}$: 1011 $\mathrm{cm^{-1}}$ in the anhydrous $\mathrm{Bu_4N^+}$ salt and 980 $\mathrm{cm^{-1}}$ in the hydrated salt.) The lower frequency for our compound suggests that the cation radical is perhaps co-ordinated (as a positive ion) to the $\mathrm{Mo^V}$ rather than simply serving as a cation.

The visible–u.v. spectrum [MeCN–$\mathrm{CHCl_3}$ (1 : 40)] showed major bands at 519, 437, 315, 272, and 251 nm. The radical cation prepared in 96% $\mathrm{H_2SO_4}$ was reported to exhibit bands at 515, 437, and 271 nm in this solvent.[3] The 251 nm band originates from the oxomolybdenum(V) species.

The solid state e.s.r. spectrum exhibits one fairly broad asymmetric signal, $\langle g \rangle$ *ca.* 1·98, but the solution spectrum [MeCN–$\mathrm{CHCl_3}$ (1 : 40)] clearly shows the presence of both the free-radical lone electron [$\langle g \rangle$ 2·0067] and the $\mathrm{Mo^V}$ lone electron [$\langle g \rangle$ 1·9500] (Figure). Spin concentration evaluation of the e.s.r. signal of the solid, using $\mathrm{K_3Mo(CN)_8}$ as standard, has shown that the signal corresponds roughly to two electrons per molecule. Since $\mathrm{Mo^V}$ compounds generally exhibit magnetic moments lower than the spin-only value (owing to spin–orbit coupling) the magnetic moment observed for our solid by the Gouy method at ambient temperature, μ_{eff} 2·0 B.M., also suggests the presence of more than one unpaired electron per molecule. Antiferromagnetic or other spin–spin and spin–orbit effects may account for the actual value, but the e.s.r. results leave no doubt about the presence of two separate unpaired electrons in the molecule. The e.s.r. spectrum of the free radical has been studied before,[3,4] but our compound is the first pure crystalline solid containing both the cation free radical and a paramagnetic metal ion which exhibits an e.s.r. signal.



FIGURE

This work was supported by a grant from the National Science Foundation.

(*Received*, 20*th November* 1972; *Com.* 1940.)

---

[1] J. Selbin, D. G. Durrett, H. J. Sherrill, G. R. Newkome, and M. Collins, submitted for publication.

[2] J. G. Scane and R. M. Stephens, *Proc. Phys. Soc.*, 1967, **92**, 833.

[3] H. J. Shine and E. E. Mach, *J. Org. Chem.*, 1965, **30**, 2130.

[4] For example, B. C. Gilbert, P. Hanson, R. O. C. Norman, and B. T. Sutcliffe, *Chem. Comm.*, 1966, **161**; C. Jackson and N. K. D Patel, *Tetrahedron Letters*, 1967, **24**, 2255; P. D. Sullivan and J. R. Bolton, *J. Magnetic Resonance*, 1969, **1**, 356; and refs. therein.