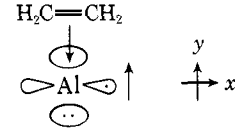
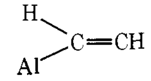
Aluminum Atom-Acetylene Adduct: Matrix Isolation Electron Spin Resonance Study

Sir:

Recently we have shown that Al atoms and ethylene molecules cotrapped in rare gas matrices react to form the complex depicted below.[1] The electron spin resonance (ESR) analysis revealed that two dative bonds are invoked for its formation:



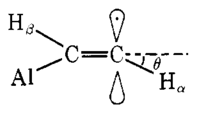
one resulting from migration of electrons from the bonding π orbital of the olefin into the vacant s-p_y orbital of Al, and the other from back-donation from the semifilled p_x orbital of Al into the antibonding π orbital. One is thus enticed to predict the formation of a complex between Al atom and acetylene based upon the identical bonding scheme. We report, in this communication, the generation and the detection by ESR of the Al atom-acetylene *adduct* stabilized in neon matrices. Contrary to the expectation the adduct was found to have the vinyl structure.



The experimental set-up designed to trap high temperature vapor phase species in a rare gas matrix at liquid helium temperature and to observe the ESR of the resulting matrix has been described earlier.[2] In the present series of experiments Al atoms were vaporized from a resistively heated tantalum cell and trapped in neon matrices together with acetylene introduced through a separate gaseous sample inlet. The compositions of the matrices were roughly 1000:10:1 for neon atoms, acetylene molecules, and Al atoms, respectively. The frequency of the spectrometer locked to the sample cavity was 9.410 GHz.

As reported previously, a neon matrix containing Al atoms alone appears white and shows no ESR signal.[1] A neon matrix containing both Al and acetylene appeared purple and showed a strong ESR signal centered about the position corresponding to g = 2.00. The spectra observed from neon matrices containing Al and C_2D_2 (perdeuterioacetylene), and Al and C_2H_2 (normal acetylene) are shown in Figures 1a and 2a, respectively. The simple sextet pattern conspicuously resolved in Figure 1a must be attributed to the hyperfine structure due to ^{27}Al (I = $5/2$, natural abundance = 100%). The systematic variation in the line widths of the successive hyperfine components can be accounted for by a small anisotropy of the Al-coupling tensor. A close inspection of Figure 2a reveals the presence of several doublet-of-doublets patterns spaced by the Al coupling as indicated. The patterns in the outer regions are obscured by the increased contribution of the anisotropy of the Al-coupling tensor.

The hyperfine coupling interactions delineated above with one ^{27}Al nucleus and two nonequivalent protons strongly suggest that the observed spectra be assigned to Al-acetylene complexes possessing the vinyl structure:



The larger doublet splitting of ~55 G is assigned to the β proton coupling and the smaller doublet splitting of ~20 G to the α proton. A larger hyperfine interaction is expected from the β proton because of a direct overlap possible between its 1s orbital and the nonbonding semifilled orbital at the α carbon.

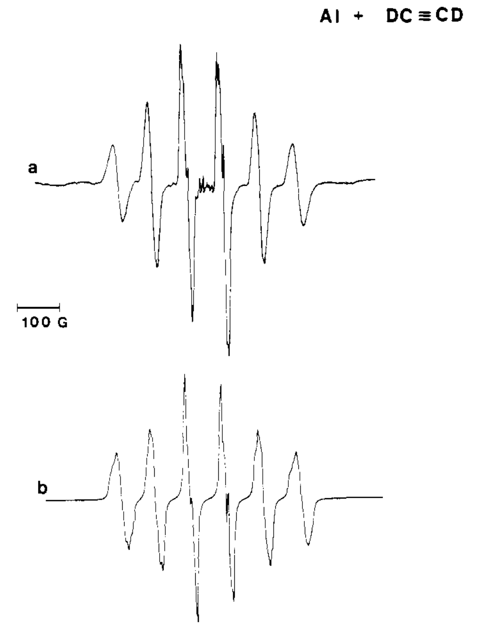


Figure 1. (a) ESR spectrum observed from neon matrix containing Al and C_2D_2. (b) Computer-simulated spectrum based upon the parameters given in the text.

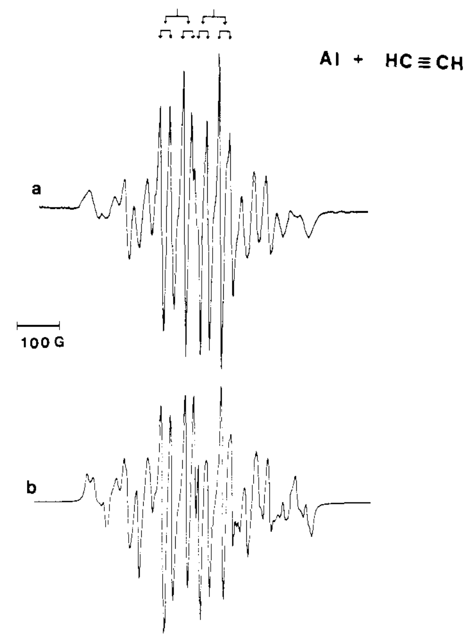


Figure 2. (a) ESR spectrum observed from neon matrix containing Al and C_2H_2. (b) Computer-simulated spectrum based upon the parameters given in the text.

Table I

	x	y	z
g	2.0005	2.0023	2.0023
Al	85 ± 1 G	92	78
H_α	25	20	15
H_β	55	55	55

Resorting to the method of computer simulation[3] (of the ESR spectra of randomly oriented radicals) the g and hyperfine coupling tensors were assessed from the observed spectra (Table I). Figures 1b and 2b are the computer-simulated spectra based upon these parameters.

The essentially isotropic hyperfine interaction with Al must also result from the direct overlap of its valence orbitals (3s and 3p) with the nonbonding semifilled orbital of the α carbon. The sign of the Al coupling tensor elements must, therefore, be positive.[4] The z axis along which the smallest Al coupling constant is observed must hence be perpendicular to the molecular plane of the complex. The smallest coupling constant to the α proton is observed also along the z axis. It follows that the elements of the α proton coupling tensor are positive and that the $C{=}C_\alpha{-}H_\alpha$ section of the complex is bent. Both EHT and INDO molecular orbital calculations showed that the complex would have the energy minimum in the transconfiguration (as shown above) at $\theta \cong 30°$.

We have also generated and observed the ESR spectra of Ga-acetylene complexes. More detailed analyses of the spectra presented here and those of other acetylene complexes will be reported shortly.

References and Notes

(1) P. H. Kasai and D. McLeod, Jr., *J. Am. Chem. Soc.*, **97**, 5609 (1975).
(2) P. H. Kasai, *Acc. Chem. Res.*, **4**, 329 (1971).
(3) P. H. Kasai, *J. Am. Chem. Soc.*, **94**, 5950 (1972). The high nuclear spin of Al ($I = \frac{5}{2}$) and the large hyperfine interaction with it necessitated the inclusion of the second-order terms in the simulation program.
(4) For the analyses of hyperfine coupling tensors, see, for example, P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, Amsterdam, 1967.
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Superoxotetraphenylporphinatozinc(1−)

Sir:

Synthesis of dioxygen complexes of metalloporphyrins has been the goal of several laboratories in recent years. Interest in these complexes is motivated by the desire to understand the coordination chemistry of dioxygen in complexes which resemble hemoproteins and enzymes. Recent successes have included syntheses of Ti(OEP)(O$_2$),[1] believed to contain Ti(IV) and O$_2^{2-}$;[2] Cr(TPP)(py)(O$_2$), believed to contain Cr(III) and O$_2^-$;[3] Mn(TPP)(O$_2$), believed to contain Mn(IV) and O$_2^{2-}$;[4] Fe(TpivPP)(base)(O$_2$), believed to contain Fe(III) and O$_2^-$;[5] and Co(TPP)(base)(O$_2$), believed to contain Co(III) and O$_2^-$.[6] Except for the Ti complex, which is prepared by reaction of benzoyl peroxide with Ti(OEP)(O),[2] the other metalloporphyrin dioxygen complexes are prepared by oxidative addition of dioxygen to a lower oxidation state of the metalloporphyrin, resulting in superoxo or peroxo complexes as products.[7] Preparation of superoxo or peroxo complexes of nonredox metals such as Zn^{2+} is not feasible by such a method. Instead it is necessary to use the superoxide or peroxide anions themselves as starting materials. Such a preparative route has the advantage that it allows one to assess the properties of the ligand from the point of view of a simple complexation reaction. In this communication we report the first preparation of a superoxo complex in which superoxide is used as a starting material.

Zn(TPP) binds one (and only one) axial ligand,[8-13] which may be either neutral or anionic. The bonding is believed to be primarily electrostatic in character as might be expected for a d^{10} metal ion.[10] It is therefore perhaps not surprising that Zn(TPP) reacts with superoxide to form a superoxo complex. Solutions of Zn(TPP) in benzene or toluene are red-pink. Addition of KO$_2$ solubilized by means of dicyclohexyl-18-crown-6[14] causes the solutions to become blue-green and the spectral changes can be monitored by means of visible spectroscopy.[15] The resulting spectrum is very similar to that obtained by reacting Zn(TPP) with [CH$_3$(CH$_2$)$_3$]$_4$NOH, KOC(CH$_3$)$_3$, or NaOC$_6$H$_5$.[15] Superoxide, as well as these other ions, can be displaced by addition of an excess of pyridine.[16] Addition of methanol, which is known to react with superoxide ($2CH_3OH + 2O_2^- \rightarrow O_2 + H_2O_2 + 2CH_3O^-$),[17] results in the visible spectrum obtained for Zn(TPP) in methanol-toluene mixtures (Scheme I). These observations indicate that the porphyrin is not irreversibly modified by superoxide.

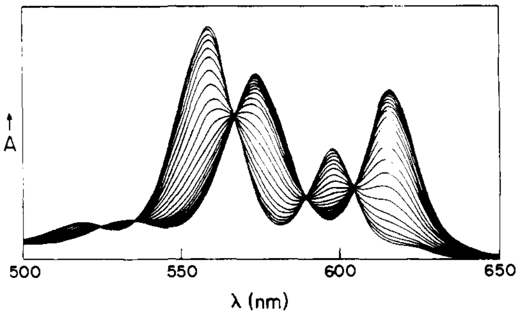
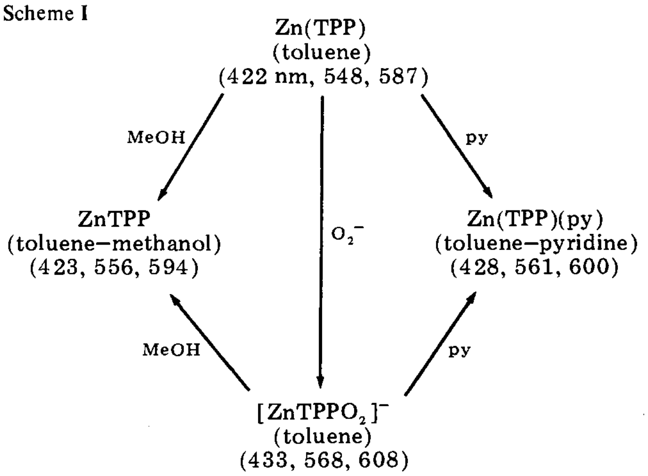


Figure 1. Visible spectra resulting from successive additions of O$_2^-$ to ZnTPP (λ_{max} 558 nm). Starting concentration of ZnTPP is 4×10^{-5} M. Final concentration of O$_2^-$ is 1×10^{-3} M. Volume is held essentially constant. Solvent is Me$_2$SO.

Scheme I



The reaction of O$_2^-$ with Zn(TPP) can also be observed in Me$_2$SO (Figure 1). Hydroxide also complexes with Zn(TPP) in Me$_2$SO, but other anions such as alkoxide, chloride, or bromide which bind in toluene do not bind in Me$_2$SO. Me$_2$SO forms a relatively stable complex with Zn(TPP) (we measure $K_{\text{equilib}} = 545$ for Zn(TPP) + Me$_2$SO $\rightleftarrows$ Zn(TPP)(Me$_2$SO) in benzene at 25 °C). Thus superoxide must have a high affinity for Zn(TPP), since it can successfully compete with Me$_2$SO even when Me$_2$SO is solvent! Unfortunately we have not been able to obtain reliable equilibrium constants because of the moisture sensitivity of O$_2^-$ or [Zn(TPP)(O$_2$)]$^-$ and because the decomposition product (possibly [Zn(TPP)OH]$^-$) has a visible spectrum similar to that of the superoxo complex.

Visible spectral results were confirmed by EPR studies at 77 K. Superoxide has a characteristically anisotropic EPR spectrum[14,18] (Figure 2a, $g_\parallel = 2.11$, $g_\perp = 2.00$). Addition of Zn(TPP) to Me$_2$SO solutions of superoxide results in a shift of the $g_\parallel$ peak to 2.07 (Figure 2b). In benzene-Me$_2$SO mixtures (4:1 by volume), where K_{equilib} for binding of O$_2^-$ is higher, the spectrum of [Zn(TPP)(O$_2$)]$^-$ can be seen with very little free superoxide apparent (Figure 2c). Addition of pyridine to Me$_2$SO or benzene-Me$_2$SO solutions of [Zn(TPP)-