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 ($I = 5/2$) 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.
(5) On leave from Department of Chemistry, University of Tokyo.

Paul H. Kasai,* D. McLeod, Jr., T. Watanabe[5]
Union Carbide Corporation, Tarrytown Technical Center
Tarrytown, New York 10591

Received January 20, 1977

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 $[CH_3(CH_2)_3]_4NOH$, $KOC(CH_3)_3$, or $NaOC_6H_5$.[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.

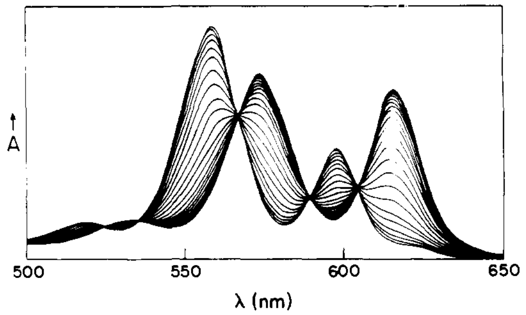
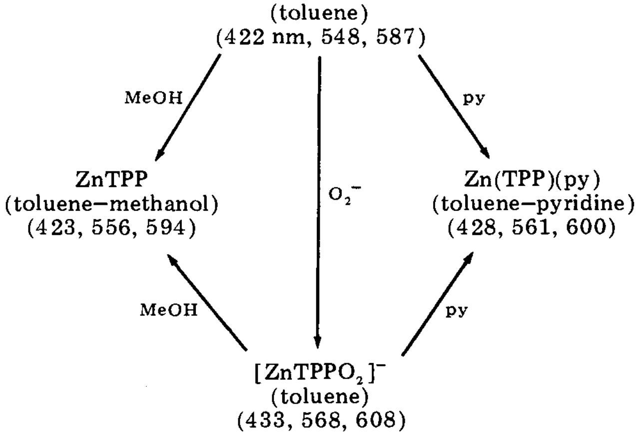


Figure 1. Visible spectra resulting from successive additions of O_2^- to ZnTPP (λ_{max} 558 nm). Starting concentration of ZnTPP is 4×10^{-5} M. Final concentration of O_2^- is 1×10^{-3} M. Volume is held essentially constant. Solvent is Me_2SO.

Scheme I



The reaction of O_2^- with Zn(TPP) can also be observed in Me_2SO (Figure 1). Hydroxide also complexes with Zn(TPP) in Me_2SO, but other anions such as alkoxide, chloride, or bromide which bind in toluene do not bind in Me_2SO. Me_2SO forms a relatively stable complex with Zn(TPP) (we measure $K_{equilib} = 545$ for Zn(TPP) + $Me_2SO \rightleftarrows$ Zn(TPP)(Me_2SO) in benzene at 25 °C). Thus superoxide must have a high affinity for Zn(TPP), since it can successfully compete with Me_2SO even when Me_2SO 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_2SO solutions of superoxide results in a shift of the $g_\parallel$ peak to 2.07 (Figure 2b). In benzene-Me_2SO 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_2SO or benzene-Me_2SO solutions of [Zn(TPP)-

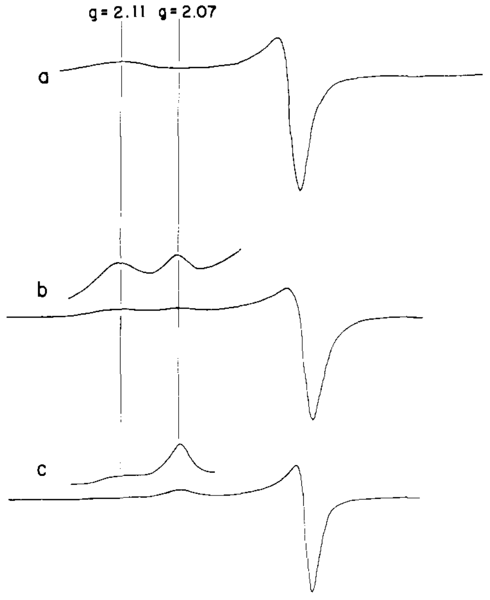


Figure 2. EPR spectra at 77 K of (a) O_2^- in Me_2SO; (b) O_2^- plus ZnTPP in Me_2SO; (c) O_2^- plus ZnTPP in benzene-Me_2SO (4:1).

$(O_2)]^-$ causes disappearance of the $g = 2.07$ peak as would be expected for displacement of coordinated O_2^- (see Scheme I). The shift of $g_\parallel$ to smaller values is expected when O_2^- is coordinated to a metal ion.[19] For example, O_2^- adsorbed on MgO has $g_\parallel = 2.077$.[19] EPR spectra of $[^{67}Zn(TPP)(O_2)]^-$[20] show a small but definite broadening (2–3 G) of the $g_\parallel$ peak. This is consistent with a highly ionic complex, i.e., little delocalization of the electron from O_2^- to Zn^{2+}.

Solid samples have been isolated from THF-hexane, which have elemental analyses consistent with the formulation K(dicyclohexyl-18-crown-6)$ZnTPPO_2$.[21] These blue powders are paramagnetic as evidenced by the fact that they have EPR spectra ($g = 2.00$) at 77 K which disappear reversibly upon warming to room temperature. Visible spectra of the dissolved solid show partial dissociation to Zn(TPP) as would be expected, since superoxide complex is formed in an equilibrium reaction. The instability of this material has hindered attempts to obtain quantitative magnetic data and IR spectra. Efforts are underway at this time to characterize these solids and to grow crystals that will be suitable for x-ray structural studies.

Acknowledgment. We are grateful to S. Barnes for preparation of $^{67}Zn(TPP)$ and to Professor James Fee and Brian Hoffman for helpful discussions. Financial support from the Rutgers Research Council, the Charles and Johanna Busch Memorial Fund, a Biomedical Sciences Support Grant, the Research Corporation, and the National Science Foundation is very gratefully acknowledged. J.S.V. also gratefully acknowledges receipt of a U.S. Public Health Service Research Career Development Award.

References and Notes

(1) Abbreviations used in this paper: OEP, octaethylporphyrin; TPP, tetraphenylporphine; py, pyridine; TpivPP, *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidophenyl) porphine; Me_2SO, dimethyl sulfoxide; THF, tetrahydrofuran; EPR, electron paramagnetic resonance.
(2) R. Guilard, M. Fontesse, P. Fournari, C. Lecomte, and J. Protas, *J. Chem. Soc., Chem. Commun.*, 161 (1976).
(3) S. K. Cheung, C. J. Grimes, J. Wong, and C. A. Reed, *J. Am. Chem. Soc.*, **98**, 5028 (1976).
(4) B. M. Hoffman, C. J. Weschler, and F. Basolo, *J. Am. Chem. Soc.*, **98**, 5473 (1976).
(5) J. P. Collman, J. I. Brauman, T. R. Halbert, and K. S. Suslick, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 3333 (1976).
(6) F. A. Walker, *J. Am. Chem. Soc.*, **92**, 4235 (1970).
(7) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976).
(8) C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).
(9) J. R. Miller and G. D. Dorough, *J. Am. Chem. Soc.*, **74**, 3977 (1952).
(10) G. C. Vogel and L. A. Searby, *Inorg. Chem.*, **12**, 936 (1973).
(11) M. D. Glick, G. H. Cohen, and J. L. Hoard, *J. Am. Chem. Soc.*, **89**, 1996 (1967).
(12) J. Fajer, D. C. Borg, A. Forman, R. H. Felton, L. Vegh, and D. Dolphin, *Ann. N.Y. Acad. Sci.*, **206**, 349 (1973).
(13) S. J. Cole, G. C. Curthoys, E. A. Magnusson, and J. N. Phillips, *Inorg. Chem.*, **11**, 1024 (1972).
(14) J. S. Valentine and A. B. Curtis, *J. Am. Chem. Soc.*, **97**, 224 (1975).
(15) λ_{max} (nm): Zn(TPP) (toluene) 422, 548, 587; $[Zn(TPP)(O_2)]^-$ (toluene) 433, 568, 608; $[Zn(TPP)(OH)]^-$ (dimethoxyethane) 432, 570, 611; $[Zn(TPP)(OC(CH_3)_3)]^-$ (toluene) 433, 569, 609; $[Zn(TPP)(OC_6H_5)]^-$ (benzene) 434, 565, 607. $[Zn(TPP)Cl]^-$ in CH_2Cl_2 gives 433, 569, 609 (see ref 12). The presence of dicyclohexyl-18-crown-6 does not affect the $[Zn(TPP)X]^-$ spectrum in any solvent used here.
(16) λ_{max} (nm): Zn(TPP)(py) (toluene) 428, 561, 600.
(17) J. SanFilippo Jr., private communication.
(18) W. Känzig and M. H. Cohen, *Phys. Rev. Lett.*, **3**, 509 (1959).
(19) J. H. Lunsford, *Catal. Rev.*, **8**, 135 (1973).
(20) $^{67}Zn(TPP)$ (^{67}Zn, $I = 5/2$) prepared from ^{67}ZnO (89.7% isotopic purity) from Oak Ridge National Laboratory.
(21) Anal. Calcd for $KZnC_{64}H_{64}N_4O_8$: C, 68.52; H, 5.76; N, 5.00; K, 3.49. Found: C, 68.43; H, 5.82; N, 4.85; K, 3.45.

Joan S. Valentine,* Y. Tatsuno, M. Nappa
Department of Chemistry, Douglass College
Rutgers, the State University of New Jersey
New Brunswick, New Jersey 08903

Received January 10, 1977

Tetrathiotetracenenickel Bis(ethylene-1,2-dithiolene). A New One-Dimensional Organic Conductor

Sir:

In the last few years the study of quasi-one-dimensional (1-D) conductors has become an important area of activity in current solid state physics research.[1] Presently, much of this interest is focused on organic π-donor-acceptor (D-A) systems with chain-like structures.[2] Despite the strong interest in such "1-D organic conductors", both the range and the absolute number of experimental systems currently available for detailed study are quite limited.

We now report the preparation and structural characterization of a new π-D-A compound which provides a unique opportunity to study 1-D electronic interactions in the presence of an internal magnetic subsystem. This compound has the empirical formula, $TTT_{1.2}NiS_4C_4H_4$, where TTT is tetrathiotetracene[3] and $NiS_4C_4H_4$ is nickel bis(ethylene-1,2-dithiolene).[4] It is the newest member of a class of π-D-A compounds derived from the interaction of bisdithiolene metal complexes with organic donor molecules[5] and the first of this class to exhibit a uniform, segregated stacking arrangement, characteristic of a 1-D organic metal.

It is obtained as small black crystals by slow cooling of a mixture of the two components in hot chlorobenzene solution.[6] Crystals measuring ca. 0.02 × 0.1 × 1.0 (mm) were used for four-probe dc conductivity measurements, EPR, and structural studies. Also, magnetic susceptibility measurements were made on an unoriented collection of these crystals using the Faraday method. The magnetic measurements show Curie–Weiss paramagnetism with an antiferromagnetic Weiss constant of ~5 K, indicative of essentially localized unpaired electrons. The magnitude of the Curie constant is that expected for one $g = 2$, $S = 1/2$ electron per $TTT_{1.2}NiS_4C_4H_4$ formula unit. EPR measurements show only one line (~50 G at ~4 K) whose g-tensor is consistent with exchange-coupled $NiS_4C_4H_4^-$ units[4,5b] in the two orientations suggested by the crystal structure solution.

The crystal structure involves separate orthorhombic subcells for the two molecules with $a_{TTT} = 2a_{NiS_4C_4H_4}$ and $b_{TTT} = 2b_{NiS_4C_4H_4}$, but with c dimensions, corresponding to the needle axis of the crystal, in the ratio $c_{NiS_4C_4H_4}/c_{TTT} = 2.40$. The consequence is that for a given volume there are 1.2 mol-