a stable complex. Since the reduction product is a structurally distorted, relatively unstable complex and has only been isolated as a five-coordinate tertiary amine adduct,[12,21] the irreversible behavior at slow scan rates is expected. The observed irreversibility is most likely due to the loss of chloride ion from the manganese(II) complex followed by solvation and ultimately decomposition of the solvated complex as shown in eq 1 and 2. Such behavior is consistent with the known

$$[\mathrm{Mn^{III}L^{2-}Cl(24\pi)}] \xrightarrow{+e^-} [\mathrm{Mn^{II}L^{2-}Cl(24\pi)}]^- \qquad (1)$$

$$\text{solvent} + [\mathrm{Mn^{II}L^{2-}Cl(24\pi)}]^- \rightarrow [\mathrm{Mn^{II}L^{2-}(24\pi)(solvent)}]^0 + \mathrm{Cl^-} \qquad (2)$$

solution behavior of the Mn(II) compound. A room-temperature ESR spectrum of the reduction product in CH_3CN gave a $g \approx 2$ transition having a six-line hyperfine coupling pattern. An identical ESR spectrum was observed for $[\mathrm{Mn^{II}L^{2-}(NEt_3)}]^0$ dissolved in acetonitrile at room temperature.[12]

The dianionic macrocyclic ligand L^{2-} stabilizes the trivalent oxidation state of manganese relative to the saturated macrocyclic system [14]aneN_4.[22] However, the dianionic ligand apparently does not sufficiently stabilize Mn(IV) to enable this species to be generated by electrochemical oxidation. Instead it is the ligand framework which is oxidized. Moreover, the manganese cation does not dimerize, as does the corresponding Ni(II) radical cation complex,[6] even though molecular models show that a five-coordinate manganese complex could undergo dimerization. The contrasting chemical behavior exhibited by the manganese(III) and nickel(II) complexes must be due to the different electronic effects exerted by the individual central metal ions.

In an effort to determine the oxidation states accessible to manganese as a function of ligand structure, we are continuing to examine the redox properties of manganese macrocyclic complexes.

Acknowledgment. We thank Dr. Michael C. Hughes for his assistance in the early stages of this work and the Syracuse University Department of Chemistry for its support.

Registry No. $[\mathrm{Mn^{III}L^0Cl(22\pi)}]^{2+}$, 61634-01-3; $[\mathrm{Mn^{III}L^{-}\cdot Cl(23\pi)}]\mathrm{PF_6}$, 61633-99-6; $[\mathrm{Mn^{III}L^{2-}Cl(24\pi)}]^0$, 56943-19-2; $[\mathrm{MnLCl}]^-$, 61634-04-6; $[\mathrm{Mn^{III}L^0Br(22\pi)}]^{2+}$, 61634-03-5; $[\mathrm{Mn^{III}L^{-}\cdot Br(23\pi)}]^+$, 61634-02-4; $[\mathrm{Mn^{III}L^{2-}Br(24\pi)}]^0$, 56943-20-5; $[\mathrm{MnLBr}]^-$, 61634-06-8; $[\mathrm{Mn^{III}L^0NCS(22\pi)}]^{2+}$, 61634-05-7; $[\mathrm{Mn^{III}L^{-}\cdot NCS(23\pi)}]^+$, 61634-08-0; $[\mathrm{Mn^{III}L^{2-}NCS(24\pi)}]^0$, 56943-21-6; $[\mathrm{MnLNCS}]^-$, 61634-07-9; $[\mathrm{MnLN_3}]^{3+}$, 61634-10-4; $[\mathrm{Mn^{III}L^0N_3(22\pi)}]^{2+}$, 61634-09-1; $[\mathrm{Mn^{III}L^{-}\cdot N_3(23\pi)}]^+$, 61634-00-2; $[\mathrm{Mn^{III}L^{2-}N_3(24\pi)}]^0$, 56943-23-8; $[\mathrm{MnLN_3}]^-$, 61634-11-5.

References and Notes

(1) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).
(2) J. Furhop, K. M. Kadish, and D. G. Davis, *J. Am. Chem. Soc.*, **95**, 5140 (1973).
(3) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).
(4) T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.*, **94**, 4529 (1972).
(5) R. H. Felton, G. S. Owen, D. Dolphin, and J. Fajer, *J. Am. Chem. Soc.*, **93**, 6332 (1971).
(6) F. C. McElroy and J. C. Dabrowiak, *J. Am. Chem. Soc.*, **98**, 7172 (1976).
(7) T. Osa and T. Kuwana, *J. Electroanal. Chem.*, **22**, 389 (1969).
(8) V. Kotovic, L. Lindoy, and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).
(9) The conductivity measurements were analogous to those made in ref 4. The various constants necessary for the calculation are found in the references cited in ref 4.
(10) F. H. Fraser and D. J. Macero, *Chem. Instrum.*, **4**, 97 (1972); F. H. Fraser, Dissertation, Syracuse University, 1972.
(11) V. L. Goedken, J. Molin-Case, and Y. A. Whang, *J. Chem. Soc., Chem. Commun.*, 337 (1973).
(12) D. R. Neves and J. C. Dabrowiak, *Inorg. Chem.*, **15**, 129 (1976).
(13) D. R. Neves, M.S. Thesis, Syracuse University, 1975.
(14) W. H. Woodruff, R. Pastor, and J. C. Dabrowiak, *J. Am. Chem. Soc.*, **98**, 7999 (1976); L. A. Nafie, R. W. Pastor, J. C. Dabrowiak, and W. W. Woodruff, *ibid.*, **98**, 8007 (1976).
(15) No M(IV) derivatives with this macrocyclic ligand have yet been reported.
(16) J. Fuhrhop, "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, New York, N.Y., 1975, p 593.
(17) Attempts to obtain the ^1H NMR spectrum of this complex were unsuccessful. It has very limited solubility ($\sim 10^{-3}$ M) in solvents which it does not react with. Examining a saturated CH_3CN solution of the compound with an ^1H FT NMR spectrometer (40 000 pulses) did not result in a spectrum.
(18) OEP is octaethylporphyrin and TPP is tetraphenylporphyrin.
(19) B. R. McGarvey, *Transition Met. Chem.*, **3**, 39 (1966).
(20) This magnetic moment as well as the variable-temperature magnetic behavior is consistent with either a Mn(IV), d^3 electronic system or an antiferromagnetically coupled Mn(III) ligand radical complex.
(21) M. C. Weiss, B. Bursten, S. Ping, V. L. Goedken, *J. Am. Chem. Soc.*, **98**, 8021 (1976).
(22) P. S. Bryan and J. C. Dabrowiak, *Inorg. Chem.*, **14**, 296, 299 (1975).

Contribution from the Department of Chemistry,
Ithaca College, Ithaca, New York 14850

Thermodynamic Study of the Adduct Formation of Zinc Tetraphenylporphine with Several Neutral Donors in Cyclohexane

Glenn C. Vogel* and James R. Stahlbush[1]

Received August 11, 1976 AIC60584N

There have been numerous studies involving the Lewis acid–base interaction between metalloporphyrins and nitrogen donors.[2-9] Of these studies, several have dealt with the metalloporphyrin zinc $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (ZnTPP).[5-7] Until recently, all thermodynamic studies involving the interaction of ZnTPP with various Lewis bases have used only nitrogen donors. In a recent study[10] the thermodynamic parameters for the adduct formation between ZnTPP and sulfur, oxygen, and phosphorus donors in the solvent benzene were reported. For the bases studied, the enthalpies of adduct formation increase in the order $S < O < P < N$. Since this order is the same as the order of donor strengths toward Lewis acids in which the electrostatic contribution to the bonding dominates the covalent contribution, it was proposed that ZnTPP should also fall into this category.

The enthalpy of adduct formation measured in the gas phase or poorly solvating media is a measure of the strength of the bond formed between a Lewis acid and base.[11] Since benzene is a basic solvent,[12] the interpretation of the enthalpies measured in benzene is more complex than those measured in poorly solvating media due to specific interactions between ZnTPP and benzene. In this note we report the first study of the thermodynamics of adduct formation of ZnTPP with nitrogen, oxygen, and sulfur donors in a noncoordinating and nonpolar solvent, cyclohexane. These solvation-minimized enthalpies[11] for the ZnTPP adducts allow us to incorporate this acid into the *E* and *C* correlation[13,14] and compare this acid quantitatively with other acids.

Experimental Section

Tetraphenylporphine and zinc tetraphenylporphine were synthesized by literature methods.[15,16] The ZnTPP was purified by dry-column chromatography.[10,16] Eastman tetrahydrothiophene (THTP) was refluxed over calcium hydride for 3 h and distilled from lithium aluminum hydride. Fisher Spectranalyzed pyridine was dried over barium oxide for 2 days and then distilled from fresh barium oxide at a pressure of 145 Torr (bp 65 °C). Chemicals Procurement Laboratories, Inc., 7-oxabicyclo[2.2.1]heptane (bridge ether) was stored over calcium hydride for 1 day and then distilled from fresh calcium hydride. Fisher Spectranalyzed dimethyl sulfoxide (Me_2SO) was dried over Linde 4A molecular sieves for 1 week and then distilled from calcium hydride at 30 Torr (bp 67 °C). Care must be taken during distillation due to vigorous bumping of Me_2SO. Fisher Spectranalyzed cyclohexane was stored over Linde 4A molecular sieves as were the purified bases.

Due to the limited solubility of ZnTPP in cyclohexane, the concentration of ZnTPP was initially determined using a Perkin-Elmer

Table II. Thermodynamic Results for ZnTPP-Donor Systems[a]

Donor	λ, nm	K, L/mol	$-\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol K)	$-\Delta H$,[b] kcal/mol
Pyridine ($E_B = 1.17$, $C_B = 6.40$)[c]	416.2	25 300	10.1 ± 0.3	13.7 ± 1.1	
	426.1	24 800	10.0 ± 0.3	13.5 ± 0.9	
	d	25 100	10.0 ± 0.2	13.5 ± 0.7	10.0
Me_2SO ($E_B = 1.34$, $C_B = 2.85$)[c]	416.2	3 840	8.7 ± 0.1	12.8 ± 0.3	
	424.7[e]	3 800	8.5 ± 0.4	12.2 ± 1.4	
	d	3 820	8.7 ± 0.1	12.8 ± 0.4	8.7
Bridge ether ($E_B = 0.887$, $C_B = 4.11$)[f]	416.2	459	7.1 ± 0.4	11.6 ± 1.3	
	422.5	492	7.2 ± 0.4	11.7 ± 1.3	
	d	475	7.1 ± 0.4	11.7 ± 1.3	7.1
THTP ($E_B = 0.341$, $C_B = 7.90$)[c]	416.2	97.0	7.0 ± 0.4	14.3 ± 1.2	
	427.5	92.1	6.4 ± 0.6	12.5 ± 2.0	
	d	94.5	6.7 ± 0.4	13.4 ± 1.3	6.7

[a] Temperature 298 K. [b] Calculated from eq 1 using E_A and C_A numbers of 5.15 and 0.624, respectively, for ZnTPP. [c] E and C numbers taken from ref 11. [d] Thermodynamic parameters determined using data from both wavelengths. [e] Only three temperatures used for this wavelength. [f] E and C numbers for donor from private correspondence with Professor R. S. Drago, University of Illinois.

103 atomic absorption spectrometer and an extinction coefficient for ZnTPP was determined. All further concentrations of ZnTPP were determined using this extinction coefficient.

The absorbance measurements were made on a Cary Model 14 UV-visible spectrophotometer with a thermostated cell compartment. Measurements were made at two wavelengths in the Soret region of the spectra at temperatures from 15 to 35 °C at approximate intervals of 5 °C, using quartz cells with a 1-cm path length. The procedure used for the treatment of data has been reported.[10,17] The Soret red shifts were measured in cyclohexane by adding the minimum amount of donor needed to completely complex ZnTPP.

Results and Discussion

The extinction coefficient determined for ZnTPP in cyclohexane at 416.2 nm is 7.52×10^5 M^{-1} cm^{-1}. The presence of only one species in solution was established for ZnTPP for the concentration range of 10^{-7} to 10^{-5} M by obtaining a Beer's law plot. The spectroscopic data for all ZnTPP–base systems are listed in Table I available as supplementary material. The thermodynamic parameters obtained from van't Hoff plots are listed in Table II.

Previous work with the ZnTPP–pyridine system has shown that a 1:1 complex is formed.[5,7] The formation of a 1:1 complex is reasonable since it has been shown by x-ray crystallography that the Zn^{2+} ion lies out of the plane of the porphyrin skeleton and therefore favors a square-pyramidal coordination.[18] The results obtained in this study are consistent with these findings. The enthalpies from Table II for the donors studied increase in the order S < O < N. These results are in agreement with a previous study[10] for ZnTPP with several donors but in the solvent benzene. The entropy changes accompanying the adduct formation are constant within the experimental errors and have the same magnitude and sign as those observed in the previous work.

Comparing the enthalpy obtained spectroscopically by Miller and Dorough[5] of −9.2 ± 0.1 kcal/mol for ZnTPP toward pyridine in benzene with the enthalpy for the same interaction but in cyclohexane, one obtains a difference of 0.8 kcal/mol. This difference may be attributed to the interaction of benzene with pyridine. Enthalpies of adduct formation determined by the calorimetric procedure yield pyridine heats in benzene that are always ~1 kcal/mol less exothermic than the corresponding heats measured in alkane solvents.[12] In addition, it is interesting to note that the enthalpy predicted by the E and C equation (vide infra) for ZnTPP and benzene forming a 1:1 adduct is −1.4 kcal/mol. The combined effect of both interactions with benzene predicts a larger difference between the enthalpies for the ZnTPP–py system measured in the two solvents. However, it has recently been demonstrated that when enthalpies of adduct formation are determined *spectroscopically*, the heat of interaction between the solvent and the solute may not contribute its complete enthalpic effect to the measured enthalpy if the interaction between the solvent and solute is small.[11]

When the enthalpies of an acid–base interaction are measured in the gas phase or in a poorly solvating solvent, one can correlate the enthalpies by the equation

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

which was proposed in 1965 by Drago and Wayland.[13] The E_A and E_B parameters are interpreted as the susceptibility of the acid and base, respectively, to undergo electrostatic interaction. The C_A and C_B parameters are interpreted as the susceptibility of the acid and base, respectively, to undergo covalent interaction. At present there are no metalloporphyrins and only one zinc-containing acid incorporated into the E and C correlation.[14] The measured enthalpies reported in Table II allowed ZnTPP to be incorporated into the correlation by the general procedure previously described.[19] Since the enthalpies obtained at the two different wavelengths are the same within experimental error, the average values of the enthalpies were employed in obtaining E_A and C_A parameters for ZnTPP. The parameters calculated for ZnTPP are $E_A = 5.15 \pm 0.13$ and $C_A = 0.624 \pm 0.038$. Table II contains the donors, their E_B and C_B parameters, and the enthalpies calculated using eq 1. The agreement between the calculated and measured enthalpies is excellent.

Figure 1 is a plot of the simultaneous equations which were solved to produce the E and C fit.[14] As can be seen in Figure 1, the slopes of the various lines for the donors used are significantly different indicating that donors with a wide range of C/E ratios were used. As Figure 1 indicates, the E and C values for ZnTPP are very dependent on the enthalpy toward THTP. Since the THTP enthalpy has the greatest uncertainty of the four values reported (see Table II), the error limits have been assigned to the E and C parameters of ZnTPP to cover the uncertainty in the enthalpy toward THTP. Consequently, the error limits assigned to the parameters of ZnTPP are larger than the marginal standard deviation normally reported.[14]

Previous work suggested that ZnTPP can be classified as an acid with a small C/E ratio.[10] The present work indicates that ZnTPP has a C/E ratio similar to those of hydrogen-bonding acids, but the magnitude of both parameters is generally larger than those of the corresponding parameters of these acids.[15] The only H-bonding acid in the E and C correlation with both E and C values larger is hexafluoroisopropyl alcohol. The small C/E ratio might indicate that the interaction between ZnTPP and the donor is largely dipole–dipole as a result of the Zn^{2+} ion lying out of the plane of the porphine skeleton[18] and the absence of low-energy d

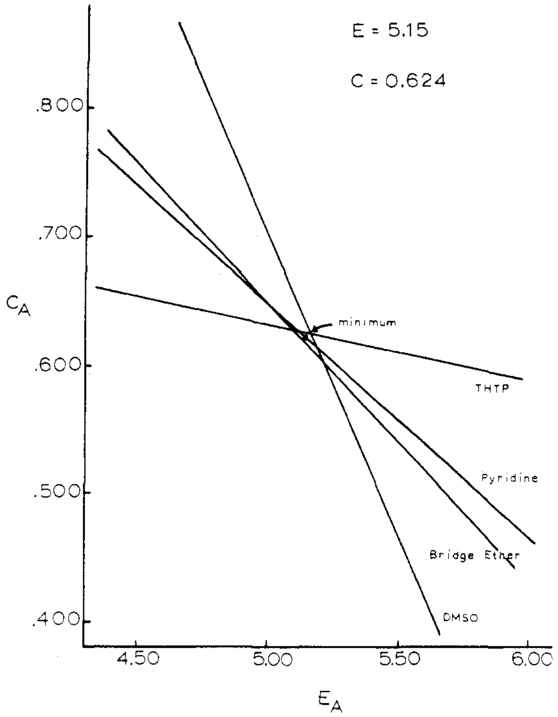

Figure 1. Plot of the two variables in eq 1 for zinc tetraphenylporphine.

orbitals to participate in a covalent interaction.

The other Zn-containing acid presently in the E and C correlation is bis(hexamethyldisilylamino)zinc(II), $Zn[N(SiMe_3)_2]_2$, with $C = 1.07$ and $E = 5.16$.[20] The difference between the acids is that the C value for ZnTPP is smaller and, consequently, $Zn[N(SiMe_3)_2]_2$ is a stronger acid than ZnTPP toward all donors because their E parameters are essentially identical. In addition, $Zn[N(SiMe_3)_2]_2$ undergoes extensive reorganization upon adduct formation, while apparently the ZnTPP does not. The energy spent in the course of converting the hexamethyldisilylamino groups from a linear free acid toward the trigonal geometry in the adduct must vary with the strength of the interaction and is incorporated into the E and C parameter of the acid. On the other hand, for ZnTPP the zinc lies somewhat out of plane in the four-coordinate ZnTPP species and little reorganization energy is required upon adduct formation.

For metalloporphyrins it has been observed that the maximum of the Soret band shifts to longer wavelengths upon adduct formation.[4,7,21-25] For nitrogen donors (pyridines and anilines) this Soret red shift has been shown to increase with base strength as manifested by the pK_a of the nitrogen donors.[7] It is of interest to find relationships between the spectral shift and other properties of the adduct for a greater range of donor types. Since the E and C numbers for ZnTPP have been determined, the enthalpies of adduct formation toward a wide range of donor types can be calculated. Table III contains the enthalpies of interaction toward nitrogen, oxygen, phosphorus, sulfur, and π donors along with their corresponding Soret red shifts. As can be seen, no general relationship exists between the E_B or C_B numbers and the shifts. Figure 2 shows the general trend that the spectral shift increases directly with magnitude of the interaction between ZnTPP and the donor as manifested by the enthalpies. Sulfur donors apparently do not follow the same correlation as the other donor types.

This red shift in the Soret region of the spectrum has been attributed to steric interference between the donor molecule and the π-electron system of the porphyrin ring.[21-24] Others have proposed that the dominant contribution to this spectral shift is the change in the interaction between the porphyrin and the metal ion resulting from adduct formation.[7,25] In solution it is difficult to estimate how far the zinc ion lies out of the porphyrin plane or the zinc–donor atom distance. Thus, the relative importance of steric interference in causing the red shift is not apparent from the data in Table III or Figure 2. However, as the enthalpy of adduct formation changes so does the interaction between the zinc ion and the porphyrin ligand. The binding of the donor can be expected to reduce the electronegativity of the zinc ion and, consequently, the zinc ion will serve as a less effective electron acceptor from the porphyrin nitrogens. This has been suggested as a dominant contribution to the Soret red shift.[7,25]

Table III. Soret Red Shifts and Enthalpies of Adduct Formation for ZnTPP–Donor Systems

	Donor	E_B, C_B[a]	$-\Delta H$,[b] kcal/mol	$\Delta\lambda$,[c] nm
1.	Benzene	0.11, 1.40	1.4	1.6
2.	Methyl acetate	0.903, 1.61	5.7	4.6
3.	Acetone	0.987, 2.33	6.5	5.2
4.	Ethyl acetate	0.975, 1.74	6.1	5.3
5.	Tetrahydrofuran	0.978, 4.27	7.6	6.2
6.	Bridge ether	0.887, 4.16	7.1	6.3
7.	4-Ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane	0.548, 6.41	6.8	6.2
8.	Me_2SO	1.34, 2.85	8.7	8.5
9.	Dimethylacetamide	1.32, 2.58	8.4	8.8
10.	Trimethyl phosphite	1.03, 5.99	9.0	9.5
11.	Pyridine	1.17, 6.41	10.0	9.9
12.	Triethylamine	0.991, 11.09	12.0	10.1
13.	Hexamethylphosphoramide	1.52, 3.55	9.9	10.4
14.	1-Azabicyclo[2.2.2]octane	0.704, 13.2	11.8	11.1
15.	THTP	0.341, 7.90	6.7	11.8
16.	Diethyl sulfide	0.339, 7.40	6.4	11.2
17.	Pentamethylene sulfide	0.375, 7.40	6.4	11.4

[a] E and C numbers taken from ref 11. Those for benzene and bridge ether were obtained from private correspondence with Professor R. S. Drago, University of Illinois. [b] All enthalpies calculated from eq 1, except those for bridge ether, Me_2SO, pyridine, and THTP which were measured in this study. [c] Soret red shift relative to the Soret band at 416.2 nm for ZnTPP in cyclohexane.

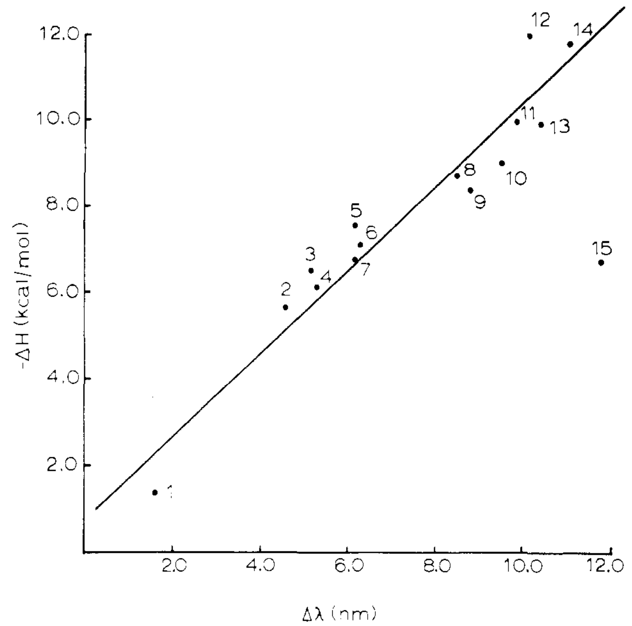

Figure 2. Plot of the enthalpy of adduct formation, ΔH, vs. the Soret red shift, $\Delta\lambda$. The numbers refer to the donors listed in Table III.

Acknowledgment. The authors wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support and Professor R. S. Drago, University of Illinois, for helpful comments.

Registry No. ZnTPP, 14074-80-7; benzene, 71-43-2; ZnTPP–methyl acetate, 61483-53-2; ZnTPP–acetone, 61483-54-3; ZnTPP–ethyl acetate, 61477-51-8; ZnTPP–tetrahydrofuran, 61477-52-9; ZnTPP–bridge ether, 61484-37-5; ZnTPP–4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, 61477-53-0; ZnTPP–Me_2SO, 61483-89-4; ZnTPP–dimethylacetamide, 61477-54-1; ZnTPP–trimethyl phosphite, 61477-55-2; ZnTPP–pyridine, 24389-79-5; ZnTPP–triethylamine, 61484-36-4; ZnTPP–hexamethylphosphoramide, 61477-56-3; ZnTPP–1-azabicyclo[2.2.2]octane, 61477-57-4; ZnTPP–THTP, 61477-58-5; ZnTPP–diethyl sulfide, 61477-59-6; ZnTPP–pentamethylene sulfide, 61477-60-9.

Supplementary Material Available: Table I containing the spectroscopic data for the ZnTPP–donor systems (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) NSF Undergraduate Research Participant, Summer 1975; PRF Undergraduate Research Participant, 1976.
(2) P. Hambright in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, pp 233–278.
(3) G. C. Vogel and B. A. Beckmann, *Inorg. Chem.*, **15**, 483 (1976).
(4) B. D. McLees and W. S. Caughey, *Biochemistry*, **7**, 642 (1968).
(5) J. R. Miller and G. D. Dorough, *J. Am. Chem. Soc.*, **74**, 3977 (1952).
(6) C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).
(7) S. J. Cole, G. C. Curthroys, E. A. Magnusson, and J. N. Phillips, *Inorg. Chem.*, **11**, 1024 (1972).
(8) (a) S. J. Cole, G. C. Curthroys, and E. A. Magnusson, *J. Am. Chem. Soc.*, **92**, 2991 (1970); (b) S. J. Cole, G. C. Curthroys, and E. A. Magnusson, *ibid.*, **93**, 2153 (1971).
(9) F. A. Walker, E. Hui, and J. M. Walker, *J. Am. Chem. Soc.*, **97**, 2390 (1975).
(10) G. C. Vogel and L. A. Searby, *Inorg. Chem.*, **12**, 936 (1973).
(11) R. S. Drago, *Struct. Bonding (Berlin)*, **15**, 73 (1973).
(12) R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Am. Chem. Soc.*, **94**, 90 (1972); M. S. Nozari and R. S. Drago, *ibid.*, **94**, 6877 (1972).
(13) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).
(14) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971).
(15) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 475 (1968).
(16) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
(17) T. J. Beugelsdijk and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 6466 (1975).
(18) D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.*, **92**, 3261 (1970).
(19) R. L. Courtright, R. S. Drago, J. A. Nusz, and M. S. Nozari, *Inorg. Chem.*, **12**, 2809 (1973).
(20) K. J. Fisher and R. S. Drago, *Inorg. Chem.*, **14**, 2804 (1975).
(21) A. H. Corwin, D. G. Whitten, E. W. Baker, and G. G. Kleinspehn, *J. Am. Chem. Soc.*, **85**, 3621 (1963).
(22) E. W. Baker, M. S. Brookhart, and A. H. Corwin, *J. Am. Chem. Soc.*, **86**, 4587 (1964).
(23) C. B. Storm, A. H. Corwin, R. R. Arellano, M. Martz, and R. Weintraub, *J. Am. Chem. Soc.*, **88**, 2525 (1966).
(24) A. H. Corwin, A. B. Chivvis, R. W. Poor, D. G. Whitten, and E. W. Baker, *J. Am. Chem. Soc.*, **90**, 6577 (1968).
(25) W. S. Caughey, H. Eberspalcher, W. H. Fuchsman, S. McCoy, and J. D. Alben, *Ann. N.Y. Acad. Sci.*, **153**, 722 (1969).

Contribution from the Wright and Rieman Chemistry
Laboratories, Rutgers, The State University of New Jersey,
New Brunswick, New Jersey 08903

Lattice Dynamics, Vibrational Anisotropy, and Hyperfine Interactions in $Sn^{II}(C_5H_7O_2)_2$

Rolfe H. Herber* and Ann E. Smelkinson

Received August 24, 1976 AIC606122

The synthesis and some properties of a number of tin(II) bis(1,3-diketonates) were reported a few years ago by Wakeshima and Kijima[1] and by Bos et al.,[2] and extensive information pertaining to these and related compounds has been published in the organometallic literature.[3] Among the properties which have been reported are the ^{119}Sn Mössbauer parameters at liquid nitrogen temperature[2,4,5] but these data have been considered only in a phenomenological manner to confirm the oxidation state assignment of the metal atom in these compounds.

Table I. ^{119}Sn Mössbauer Data for $Sn^{II}(C_5H_7O_2)_2$

Sample	Temp, K	IS, mm s^{-1}	QS, mm s^{-1}	ln [$A(T)$/ $A(78)$]	R
Neat solid	78	3.003	1.926	0	1.048
	90	3.028	1.928	−0.3391	1.087
	100	2.998	1.932	−0.7309	1.110
	110	2.982	1.936	−0.9087	1.123
	120	3.021	1.940	−1.248	1.138
	130	2.967	1.942	−1.459	(1.098)
	140	2.971	1.945	−1.766	1.176
	150	2.950	1.944	−1.991	1.183
30% v/v in butylbenzene	78	3.051	1.951		1.077

In a recent publication[6] from this laboratory the lattice dynamics and vibrational anisotropy of the related Sn(IV) compound $(CH_3)_2Sn(C_5H_7O_2)_2$ have been discussed in some detail, and in this context it was considered useful to examine related properties of $Sn^{II}(C_5H_7O_2)_2$ [$Sn^{II}(acac)_2$] in order to gain a clearer understanding concerning the geometry and bonding properties of the acetylacetonate ligand in these two species. In contrast to $(CH_3)_2Sn(acac)_2$, a solid at room temperature, for which an accurate single-crystal x-ray diffraction study[7] had provided detailed structural information and thermal parameters for the atomic motion at room temperature, the Sn(II) compound is an air- and moisture-sensitive liquid, and thus only indirect data concerning its structure have been published. In the present investigation, the lattice dynamical and hyperfine interaction parameters for this compound have been obtained over the temperature range $78 \le T \le 150$ K in order to elucidate the details of the bonding and intermolecular forces both in the neat (frozen) liquid and in glassy matrix samples of this material.

Experimental Section

$Sn^{II}(acac)_2$ was prepared by the method of Bos et al.[2] under dry nitrogen to yield a golden yellow oil which was freed of excess solvent by vacuum distillation. The reaction product was transferred to an anhydrous, N_2-filled glovebox and samples for Mössbauer effect studies were transferred in an inert atmosphere, using a hypodermic syringe, into Mylar window fitted copper cells and immediately cooled to 78 K before mounting in the spectrometer.

The Mössbauer data were acquired as described earlier.[8] Temperature control was maintained to better than ±1 K using an Artronix Model 5301 proportional temperature controller and a Pt resistance thermometer as sensor. Temperature measurement was effected using NBS-calibrated thermocouples having a sensitivity of $\sim 20\ \mu V/deg$. Spectrometer calibration was effected using the magnetic hyperfine splitting in NBS SRM 0.8-mil metallic iron foil.[9] All isomer shifts discussed in this paper are with reference to the resonance maximum observed using a high-purity $BaSnO_3$ absorber at 294 ± 1 K, employing the same $BaSn^{*}O_3$ source as used in the data runs.

Proton NMR spectra were obtained on $CDCl_3$ solutions in sealed tubes using a Varian T60 spectrometer with TMS as an internal standard, at room temperature, and the results were in good agreement with the values reported in the literature.[5]

Results and Discussion

The ^{119}Sn Mössbauer spectrum consists of a well-resolved doublet having an isomer shift of 3.015 ± 0.010 mm s^{-1} and a quadrupole splitting of 1.926 ± 0.015 mm s^{-1} at 78 K. These data are in reasonable agreement with those reported by Ewings et al.[5] and Bos et al.[2] (the latter corrected for the isomer shift of α-Sn). The resonance parameters over the temperature range $78 \le T \le 150$ K are summarized in Table I. Above 150 K the resonance effect magnitude becomes too small to permit accurate data reduction, even with an excess of 2×10^6 counts accumulated per velocity point in the spectrum.

The temperature dependence of the area under the resonance curve (normalized to the 78-K value) is summarized in the semilogarithmic plot shown in Figure 1. A linear