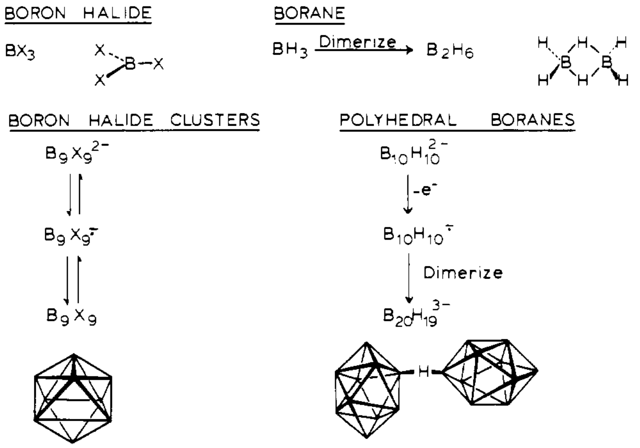

Figure 4. Electron-deficient species in boron hydrides and boron halides.

three-center BHB bonds.[14] Similarly, $B_{12}H_{12}^{2-}$ can be electrolytically oxidized to give the $B_{24}H_{23}^{3-}$ species.[15] Only the transient radical $B_8H_8^{-}\cdot$ reported by Muetterties seemed to remain monomeric at least in ethereal solvents.[16] The B_9X_9 boron halide clusters, as we have seen, are sufficiently stabilized by halogen back-donation to exist as both neutral and monoanionic electron-deficient species, favoring reduction rather than adduct formation as their predominant reaction.

Experimental Section

All reactions were carried out under air- and moisture-free conditions in Schlenk glassware. Reagent grade methylene chloride was distilled from CaH_2 and CCl_4 from P_4O_{10}. $(n\text{-}Bu_4N)B_9I_9$ and $(n\text{-}Bu_4N)_2B_9I_9$ were prepared from $(n\text{-}Bu_4N)_2B_9H_9$ as reported.[11] $Tl(CF_3COO)_3$ was obtained from Aldrich Chemical Co.

Elemental analyses were performed at Schwarzkopf Microanalytical Laboratories. Infrared spectra were recorded as Nujol mulls and KBr pellets on a Perkin-Elmer 337 spectrometer. Field-desorption mass spectra were run in CH_2Cl_2 solution on a CEC 21-110B high-resolution mass spectrometer at the Massachusetts Institute of Technology.[17]

Synthesis of B_9I_9. A solution of 200 mg, 0.12 mmol, of $(n\text{-}Bu_4N)_2B_9I_9$ in 8 mL of CH_2Cl_2 was added to 400 mg, 0.74 mmol, of $Tl(TFA)_3$. The suspension was stirred to give a red-purple suspension within minutes. After 0.5 h, the solvent was removed in vacuo and the residue extracted with 2 × 20 mL of CCl_4. The combined filtrates were evaporated to dryness. The residue was washed with hexane to give 40 mg, 0.036 mmol, of dark brown, microcrystalline solid. Anal. Calcd for B_9I_9: B, 7.85; I, 92.15. Found: B, 7.94; I, 91.50.

Reduction of B_9I_9. To a solution of 20.0 mg, 0.016 mmol, of B_9I_9 in 5 mL of CH_2Cl_2 was added dropwise a solution of 5.9 mg, 0.016 mmol, of $(n\text{-}Bu_4N)I$ in 3 mL of CH_2Cl_2. A rapid color change to dark blue was observed. After solvent removal, the residue was extracted with 2 × 3 mL of ethanol and filtered to give 22.5 mg, 0.015 mmol, of dark blue $n\text{-}Bu_4NB_9I_9$ identical with an authenic sample (95% theoretical).

Competitive Redox Reactions of B_9X_9. Equivalent amounts of B_9I_9 and $(n\text{-}Bu_4N)B_9Cl_9$ were placed in a flask. CH_2Cl_2 was added and the solution stirred for 10 min. After solvent removal, the residue was extracted twice with 5 mL of CCl_4 and filtered. The residue was then washed with ether and identified as crude $(n\text{-}Bu_4N)B_9I_9$. From the CCl_4 filtrate B_9Cl_9 can be isolated. Similar reactions were carried out with other combinations of B_9X_9 and $B_9X_9^{-}\cdot$.

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Registry No. B_9I_9, 75918-65-9; B_9Br_9, 12589-31-0; B_9Cl_9, 31304-34-4; $n\text{-}Bu_4NB_9I_9$, 72403-00-0; $n\text{-}Bu_4NB_9Br_9$, 72402-95-0; $n\text{-}Bu_4NB_9Cl_9$, 72402-98-3; $(n\text{-}Bu_4N)_2B_9I_9$, 72402-94-9.

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(14) R. C. Middaugh and F. Farha, Jr., *J. Am. Chem. Soc.*, **88**, 4147 (1966).
(15) R. J. Wiersema and R. L. Middaugh, *J. Am. Chem. Soc.*, **89**, 5078 (1967).
(16) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).
(17) We thank Dr. C. E. Costello for obtaining the mass spectrum using the MIT SRRB supported facility made available by National Institutes of Health Research Grant No. RR00317 from the Biotechnology Resources Branch, Division of Research Resources (principal investigator: Professor K. Biemann).

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Kinetic Isotope Effects for Silylene Insertions into Oxygen-Hydrogen and Silicon-Hydrogen Bonds

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Silylenes, the divalent silicon species analogous to carbenes, are known to insert into a variety of heteronuclear single bonds.[1] Oxygen-hydrogen bonds of alcohols and silicon-hydrogen bonds of silanes are efficient traps for silylenes.[2-6] In this note, we report kinetic isotope effects for the insertion of photochemically generated dimethylsilylene[7] and methylphenylsilylene[8] into Si-H and O-H single bonds.

Kinetic isotope effects have been measured for the insertion of carbenes and nitrenes into various intramolecular and intermolecular traps.[9-16] In general, the observed effects, k_H/k_D, are between 1.1 and 2.5. The magnitude of k_H/k_D in these and other related studies[17-21] has been interpreted as an in-

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(1) For a recent review, see: Gaspar, P. P. In "Reactive Intermediates"; Jones, M., Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. 1, pp 229-277.
(2) Atwell, W. H. U.S. Patent 3478078, Nov 11, 1969.
(3) Gu, T.-Y. Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *184*, 7-11.
(4) Estacio, P.; Sefcik, M. D.; Chan, E. K.; Ring, M. A. *Inorg. Chem.* **1970**, *9*, 1068-1071.
(5) Gu, T.-Y. Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *195*, 29-38.
(6) Steele, K. P.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6095-6097.
(7) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325-332.
(8) Ishikawa, M.; Ishiguro, M.; Kumada, M. *J. Organomet. Chem.* **1973**, *49*, C71-C72.
(9) Watanabe, H.; Ohsawa, N.; Sudo, T.; Hirakata, K.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 27-35.
(10) Ouellette, R. J.; Marks, D. J. *J. Organomet. Chem.* **1968**, *11*, 407-414.
(11) Seyferth, D.; Cheng, Y. M. *J. Am. Chem. Soc.* **1973**, *95*, 6763-6767.
(12) Kirmse, W.; Scholz, H. D. v.; Arold, H. *Justus Liebigs Ann. Chem.* **1968**, *711*, 22-30.
(13) Goldstein, M. J.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 2293-2295.
(14) Spialter, L.; Swansiger, W. A.; Pazdernik, L.; Freeburger, M. E. *J. Organomet. Chem.* **1971**, *27*, C25-C27.
(15) Lansbury, P. T.; Briggs, P. C. *Chem. Commum.* **1969**, 1152-1153.
(16) Lwowski, W.; Maricich, T. J. *J. Am. Chem. Soc.* **1965**, *87*, 3630-3637.
(17) Carey, F. A.; Hsu, C.-L. W. *J. Organomet. Chem.* **1969**, *19*, 29-41.
(18) Kwart, H.; George, T. J. *J. Org. Chem.* **1979**, *44*, 162-164.
(19) Witson, J. C.; Benbow, J. A.; Bowie, J. H.; Prager, R. H. *J. Chem. Soc., Perkin Trans. 2* **1978**, 498-502.
(20) Kwart, H.; George, T. J.; Louw, R.; Ultee, W. *J. Am. Chem. Soc.* **1978**, *100*, 3927-3928.
(21) Lewis, E. S.; Grinstein, R. H. *J. Am. Chem. Soc.* **1962**, *84*, 1158-1161.

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Table I. Kinetic Isotope Effects (k_H/k_D) for Silylene Insertions into Oxygen-Hydrogen and Silicon-Hydrogen Bonds

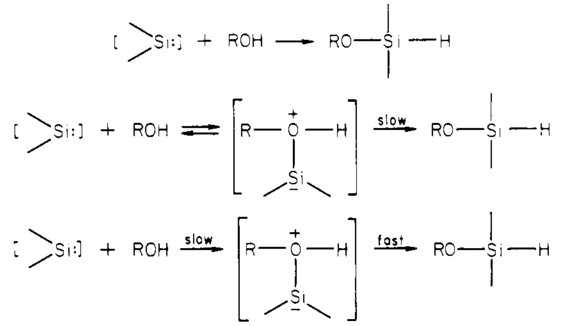
Dimethylsilylene	
ethyl alcohol/ethyl alcohol-*d*	2.33 ± 0.02 (ethyl ether)
	2.14 ± 0.18 (cyclohexane)
	2.17 ± 0.13 (THF)
tert-butyl alcohol/*tert*-butyl alcohol-*d*	1.80 ± 0.07 (ethyl ether)
n-butyldimethylsilane/ *n*-butyldimethylsilane-*d*	1.37 ± 0.09 (ethyl ether)
	1.32 ± 0.19 (cyclohexane)
Methylphenylsilylene	
tert-butyl alcohol/*tert*-butyl alcohol-*d*	1.76 ± 0.12 (ethyl ether)
	2.09 ± 0.06 (cyclohexane)

dication that the configuration of the transition state of the rate-determining step of the reaction is nonlinear or triangular. Hydrogen isotope effects for nonlinear transition states have also been treated theoretically.[22]

The kinetic isotope effects, as determined by competition experiments, for the insertion of dimethylsilylene and methylphenylsilylene into oxygen–hydrogen single bonds vary between 1.8 and 2.3 (see Table I). The effect, k_H/k_D, for the insertion of dimethylsilylene into the silicon–hydrogen single bond of *n*-butyldimethylsilane is 1.3. Isotope effects k_H/k_D are predicted to be smaller for insertion reactions into Si–H bonds[14] than into O–H single bonds.[23] These isotope effects are similar to the iostope effects observed for the other insertion reactions.[9-16] It should be noted that the isotope effects vary little with change of solvent from cyclohexane to ethyl ether to tetrahydrofuran.[6]

The occurrence and magnitude of these isotope effects support several conclusions about the mechanism of insertion of silylenes into such single bonds. The magnitude of the kinetic isotope effects observed in this study supports the proposed triangular transition state for silylene insertions.[24,25] A triangular transition state has also been proposed for the insertion of dihalocarbenes into silicon–hydrogen bonds.[26] This is consistent with the small isotope effects observed for this process.[9,14] The electrophilic silylene is believed to attack at the site of highest electron density which is the silicon–hydrogen bond in the case of the silanes. In the case of the alcohols, the oxygen atom, with two lone pairs of electrons, is the site of highest electron density. The silylene might attack the oxygen atom to form a zwitterionic intermediate which then rearranges to the dimethylalkoxysilane or methylphenylalkoxysilane via a triangular transition state. Similar zwitterionic intermediates have been proposed for the reaction of dimethylsilylene with oxetanes[27] and epoxides.[28]

There are at least three possible mechanisms for the insertion of silylenes into oxygen–hydrogen bonds of alcohols (eq 1–3). The mechanism of eq 3 is ruled out by the observed isotope effect. The rate-determining step of the reaction is the insertion of the silicon moiety into the oxygen–hydrogen bond and not the complexation of the silylene to the oxygen. Although isotope effects may arise from equilibrium isotopic fractionation of intermediate complexes,[29] there must be an equilibrium between the intermediate and some other species. Such an equilibrium is absent in eq 3. An inverse isotope effect would be predicted for a possible secondary isotope effect on



(1)

(2)

(3)

the first step of eq 3. This is not observed.

The mechanisms proposed in eq 1 and 2 are consistent with the observed isotope effects. Both mechanisms have essentially the same transition state for the rate- and product-determining step. In these cases, the isotope effects would arise from the loss of zero-point energy in the transition state leading to insertion.[30]

Mechanisms 1 and 2 are both consistent with the previously reported solvent effects.[6] With the available experimental evidence, a choice between the two mechanisms cannot be made with certainty. Presently, we favor the mechanism of eq 2 for the insertion of silylenes into O–H bands based on our experience with oxetanes and epoxides.[27,28] The mechanism of silylene insertions into Si–H bonds has been considered by several other research groups.[31-33]

Finally, the magnitude of the isotope effects reported in this note supports the view that silylenes are singlet species.[4,34,35] By analogy, the isotope effect for insertion of singlet nitrenes into carbon–hydrogen bonds is 1.5,[12] but triplet nitrenes abstract hydrogens with an isotope effect of 4.1.[36]

Experimental Section

NMR spectra were obtained on a Varian XL-100-15 spectrometer with 1% solutions of sample in chloroform-d_1. Chloroform was used as an internal standard. Samples were purified by preparative GLC on a Hewlett-Packard F&M 700 on a 25 ft × $^1/_4$ in. 20% SE-30 on Chromosorb W 60-80 mesh column. Mass spectra were run on a Hewlett-Packard 5985 GC-MS system. A 5 ft × $^1/_4$ in. 3% OV-1 on Chromosorb W 60-80 mesh column was used in the GC. Additional mass spectra were obtained on an AEI MS-9 spectrometer. All mass spectra were determined at 70 eV.

All photolyses were carried out in flame-dried 5-mm quartz NMR tubes with a medium-pressure 450-W Hanovia mercury lamp. Photolyses were run at 5 °C. No tetramethyldisiloxane, from the insertion of silylenes into adventitious water, could be detected.[3]

Isotope effects were calculated from the ratio of abundances of undeuterated to deuterated insertion products. The abundance of the deuterated product was corrected for the apparent amount of deuterated product contributed by the natural abundance of heavy isotopes in the undeuterated insertion product.[37] The abundances of the following ions were used to calculate the isotope effects: ethoxydimethylsilane, P-15 (100%); *tert*-butoxydimethylsilane, P-15 (58%); *tert*-butoxymethylphenylsilane, *tert*-P-15 (75%); *n*-butyltetramethyldisilane, P-57 (24%). These ions were of the same abundance for undeuterated and totally deuterated samples. Abundances were determined manually (AEI MS-9 spectrometer) or from the SIM and

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(22) O'Ferrall, R. A. M. *J. Chem Soc. B* **1970**, 785–790.

(23) Hine, J. "Physical Organic Chemistry"; McGraw-Hill: New York, 1962; p 72.

(24) Cox, B.; Purnell, J. H. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 859–866.

(25) Sefcik, M. D.; Ring, M. A. *J. Am. Chem. Soc.* **1973**, *95*, 5168–5173.

(26) Sommer, L. H.; Arlie Ulland, L.; Ritter, A. *J. Am. Chem. Soc.* **1968**, *90*, 4486.

(27) Gu, T.-Y. Y.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 1641–1644.

(28) Tzeng, D.; Weber, W. P. *J. Am. Chem Soc.* **1980**, *102*, 1451.

(29) Schowen, K. B. J. In "Transition States of Biochemical Processes"; Gandour, R. D.; Schowen, R. L., Eds.; Plenum Press: New York, 1978; pp 225–284.

(30) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley-Interscience: New York, 1980; pp 17–24.

(31) John, P.; Purnell, J. H. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1455–1461.

(32) Vanderwielen, A. J.; Ring, M. A.; O'Neal, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 993–998.

(33) Davidson, I. M. T. *J. Organomet. Chem.* **1970**, *24*, 97–100.

(34) Skell, P. S.; Goldstein, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 1442–1443.

(35) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 5427–5428.

(36) Hall, J. H.; Hill, J. W.; Forgher, J. M. *J. Am. Chem Soc.* **1968**, *90*, 5313–5314.

(37) Bieman, K. "Mass Spectrometry, Organic Chemical Applications"; McGraw-Hill: New York, 1962; p 60.

SPEED programs (HP-5985 system). Results from both spectrometers were consistent. Mass spectral abundances for duplicate samples are based on an average of at least six independent measurements. Control experiments showed no scrambling of deuterium occurred before or after ionization of the insertion products.

All solvents were dried over sodium benzophenone ketyl. Absolute ethanol was used without further purification. Ethyl alcohol-*d* was obtained from Merck Isotopes. *tert*-Butyl alcohol-*d* was prepared by the reaction of D_2O with lithium *tert*-butoxide. *n*-Butyldimethylsilane-d_1 was prepared by the reduction of *n*-butyldimethylchlorosilane with lithium aluminum deuteride. The isotopic composition of the reagent alcohols and silane were determined by the weights of nondeuterated and isotopically pure (as determined by IR and mass spectroscopy) deuterated reagents added.

Competition Experiments. Photolysis of Dodecamethylcyclohexasilane with Ethyl Alcohol and Ethyl Alcohol-*d* in Ethyl Ether. A typical procedure is as follows. Dodecamethylcyclohexasilane[7] (59 mg, 0.17 mmol), ethanol (142 mg, 3.09 mmol), and ethyl alcohol-*d* (160 mg, 3.33 mmol) were dissolved in 2.2 mL of dry ethyl ether and photolyzed for 90 min. Products were ethoxydimethylsilane and ethoxydimethylsilane-*d*.[3] No tetramethyldisiloxane, from the insertion of dimethylsilylene into water, could be detected.[3]

Photolysis of Dodecamethylcyclohexasilane with *tert*-Butyl Alcohol and *tert*-Butyl Alcohol-*d* in Ethyl Ether. Dodecamethylcyclohexasilane (34 mg, 0.10 mmol), *tert*-butyl alcohol (61 mg, 0.82 mmol), and *tert*-butyl alcohol-*d* (65 mg, 0.86 mmol) were dissolved in 2.3 mL of dry ethyl ether and photolyzed for 90 min. Products were *tert*-butoxydimethylsilane and *tert*-butoxydimethylsilane-*d*.[3]

Photolysis of Octamethyl-2,3-diphenyltetrasilane with *tert*-Butyl Alcohol and *tert*-Butyl Alcohol-*d* in Ethyl Ether. Octamethyl-2,3-diphenyltetrasilane[8] (90 mg, 0.23 mmol), *tert*-butyl alcohol (153 mg, 2.07 mmol), and *tert*-butyl alcohol-*d* (82 mg, 1.10 mmol) were dissolved in 2.2 mL of dry ethyl ether and photolyzed for 90 min. Products were *tert*-butoxymethylphenylsilane, *tert*-butoxymethylphenylsilane-*d*,[3] and hexamethyldisilane.

Photolysis of Dodecamethylcyclohexasilane with *n*-Butyldimethylsilane and *n*-Butyldimethylsilane-*d* in Ethyl Ether. Dodecamethylcyclohexasilane (51 mg, 0.15 mmol), *n*-butyldimethylsilane (110 mg, 0.94 mmol), and *n*-butyldimethylsilane-*d* (37 mg, 0.32 mmol) were dissolved in 2.2 mL of dry ethyl ether. Products were *n*-butyltetramethyldisilane and *n*-butyltetramethyldisilane-*d*.[5]

Control Experiments. Control experiments were run the same as competition experiments except only a deuterated trap was used.

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Registry No. Dodecamethylcyclohexasilane, 4098-30-0; octamethyl-2,3-diphenyltetrasilane, 40907-20-8; ethanol, 64-17-5; *tert*-butyl alcohol, 75-65-0; *n*-butyldimethylsilane, 1001-52-1; D_2, 7782-39-0.

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Single-Crystal EPR and Optical Spectra of and INDO-MO Calculations on Planar $Cu(NCS)_4^{2-}$

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Table I. Experimental and Calculated Spin Hamiltonian Parameters[a] for the $Cu(NCS)_4^{2-}$ Ion

	exptl values				INDO-MO based calcd values	
	powder		single crystal			
	RT	LNT	RT	LNT	planar	tetragonal
$g_\parallel$	2.275	2.279	2.272	2.274	2.190	2.255
$g_\perp$	2.053	2.053	2.056	2.056	2.036	2.048
$A_\parallel$	173 ± 2	174 ± 2	171 ± 2	171 ± 2	−169.5	−175.2
$A_\perp$			54 ± 3	54 ± 3	−63.9	−60.0

[a] Hyperfine values in 10^{-4} cm^{-1}.

The halocuprates[1] have often been used to test the application of bonding models of transition-metal complexes since they are found to exhibit a wide variety of stereochemistries. Such studies on chlorocuprates have been already reported in the literature.[1-13] Several molecular orbital (MO) calculations have also been carried out on this ion.[14-16] Several pseudohalo complexes of transition ions, particularly those of nickel and copper, follow in general the properties of the chlorocuprates such as changes in stereochemistry, and they have been studied in detail by Forster and Goodgame.[17,18] While larger cations seem to favor independent dissociated tetrahedral anion entities, smaller ones seem to allow the association of neighboring anions, resulting in a tetragonal symmetry around each metal atom. Of these, in $CuHg(SCN)_4$, the Cu^{2+} is in a tetragonal ligand field and is surrounded by four nitrogens and two sulfur atoms. Similar environment has also been reported[17] to be present for Cu^{2+} in $[(C_2H_5)_4N]_2Cu(NCS)_4$. The present study confirms the above predictions and suggests a fairly square-planar ligand field around the cupric ion. We report here the single-crystal EPR and optical spectral properties of this complex which contains planar $Cu(NCS)_4^{2-}$ groups possibly linked by axial bonds to sulfurs of the nearby molecule to produce a centrosymmetric distorted octahedral coordination geometry.

Experimetal Section

The complex tetraethylammonium tetrakis(isothiocyanato)cuprate(II) was prepared by the method of Forster and Goodgame.[17] It belongs to the orthorhombic space group *Pbca* and crystallizes as pale green plates with well-developed (100) planes when grown from a solution of nitromethane–ether maintained at a temperature of 0–5 °C. The optical spectra at room temperature (RT) and liquid-nitrogen temperature (LNT) were measured in a Carl-Zeiss DMR-21 instrument using a single-crystal mount on a cold finger. Our attempts to measure the direction of polarization failed since the unique axis of all the molecules in the unit cell was found to be along the *a*-axis direction which happens to grow too thin to permit the use of the polarized radiation. However, the EPR measurements were done in three orthogonal planes including the well-developed (100) planes by using a Varian E-4 spectrometer with a 100-kHz modulation. DPPH (g = 2.0036) was used to calibrate the g value.

Results and Discussion

When the magnetic field was in the (100) plane, the EPR

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(1) D. W. Smith, *Coord. Chem. Rev.*, **21**, 93 (1976).
(2) J. P. Steadman and R. D. Willett, *Inorg. Chim. Acta*, **4**, 367 (1970).
(3) F. Barendregt and H. Schenck, *Physica (Amsterdam)*, **49**, 465 (1970).
(4) J. Ferguson, *J. Chem. Phys.*, **40**, 3406 (1964).
(5) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).
(6) J. A. McGinnety, *J. Am. Chem. Soc.*, **94**, 8406 (1972).
(7) N. Bonamies, G. Dessey, and A. Vaciago, *Theor. Chim. Acta*, **7**, 367 (1967).
(8) A. W. Schwetler, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, **5**, 277 (1966).
(9) R. L. Harlow, W. J. Wells, G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, **13**, 2106 (1974).
(10) G. C. Allen and N. S. Hush, *Inorg. Chem.*, **6**, 4 (1967).
(11) R. Laiko, M. Natarajan, and M. Kaira, *Phys. Status. Solidi A*, **15**, 311 (1973).
(12) P. Cassidy and M. A. Hitchman, *J. Chem. Soc., Chem. Commun.*, 837 (1975); *Inorg. Chem.* **16**, 1568 (1977).
(13) M. A. Hitchman and P. Cassidy, *Inorg. Chem.*, **17**, 1682 (1978).
(14) P. Ros and G. C. A. Schuit, *Theor. Chim. Acta*, **4**, 1 (1966).
(15) J. Demuynek and A. Veillard, *Chem. Phys. Lett.*, **6**, 204 (1970).
(16) N. J. Trappeniers, G. de Brouchiere, and C. A. Ten Seldam, *Chem. Phys. Lett.*, **8**, 327 (1971).
(17) D. Forster and D. M. L. Goodgame, *Inorg. Chem.* **4**, 715, 823, 1712 (1965); **6**, 339 (1967).
(18) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 2790 (1964).