Table III. Possible A–H···B Hydrogen Bonds

A	B	A···B, Å	H···B, Å	A–H···B, deg
		$(9\text{-MeGuaH})PtCl_3\cdot H_2O$		
N1	Cl3	3.25	2.28	163
N3	Cl1	3.26	2.28	163
N11	OW	2.85	1.95	158
OW	O	2.85		
OW	Cl1	3.19		
		$(9\text{-MeGuaH})_2PtCl_6\cdot 2H_2O$		
N1	Cl1	3.25	2.25	175
N7	OW	2.67	1.65	162
N11	N3	3.06	2.15	152
OW	O	2.80	1.81	156
OW	Cl1	3.23		
OW	Cl2	3.20		

Cu(II) complexes[20,22] and the present Pt(II) complex, the angle C5–N7–C8 ranges from 104.5 to 105.0°, which is very close to the unprotonated case of 104.2°. This effect has been noted before[7] and established in Hodgson's review paper.[1b]

As is usually observed[25] in nine-atom framework of the purine is significantly nonplanar. The dihedral angle between the highly planar imidazole ring and the pyrimidine ring, which retains some degree of nonplanarity (largest deviation from the plane if 0.039 Å for C6) is 3.0°. The Pt atom is in the imidazole plane. In *the salt* the 9-methylguaninium ion is protonated at N1 and N7 and the valence angles at N1, N7, and the unprotonated N3 are in agreement with the above mentioned rule. The bond lengths and angles are in excellent agreement with those in 9-ethylguaninium ion,[8] with generally no more than twice the estimated standard deviation (0.005 Å, 0.4°) difference. Both the imidazole and the pyrimidine rings are highly planar with an angle of 2.7° between them.

Crystal Packing. The hydrogen bonding in these structures is extensive. There are many potential donor and acceptor sites and almost all of them are used. The hydrogen bonds are listed in Table III and shown in Figures 4[14] and 5.[14] The criterion used for inclusion of an interaction is that of Hamilton and Ibers,[26] who note that a A–H···B hydrogen bond probably exists if both A–H and H···B separations are less than the sum of the van de Waals radii of the two atoms. When the hydrogen position was not known, the A···B separation was used and compared with similar literature[8] values. In *the complex* long zigzag "chains" are formed in which consecutive molecules are held together by hydrogen bonds N3–H3···Cl1 and via the water molecule. The interchain hydrogen bond is N1–H1···Cl3 (Figure 4). In *the salt* the packing is quite different. Two bases form a "planar" dimer across a center of symmetry via hydrogen bonds between N3 and N11. These dimers are joined across another center of symmetry, via the water molecules, to form extended "planar" chains. Except for a weak base stacking arrangement at 3.30 Å, there is no interaction between these "planar" chains. Interspersed between these chains are the $PtCl_6^{2-}$, ions which hold the structure together via hydrogen bonds (Figure 5).

Registry No. $(9\text{-MeGuaH})PtCl_3$, 84433-30-7; $(9\text{-MeGuaH})_2PtCl_6$, 84433-31-8; K_2PtCl_4, 10025-99-7.

Supplementary Material Available: Listings of hydrogen atom parameters, observed and calculated structure amplitudes, and thermal parameters for the non-hydrogen atoms (Table IV) and packing diagrams (Figures 4 and 5) (16 pages). Ordering Information is given on any current masthead page.

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Notes

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Structural Characterization of a $B_{11}H_{11}^{2-}$ Derivative: Molecular Structure of $(C_2H_5)_4N^+B_{11}H_{10}S(CH_3)_2^-$

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and Michael G. Gatter

Received May 4, 1982

The eleven-vertex polyhedral borane $B_{11}H_{11}^{2-}$ has long been of interest due to its remarkably facile fluxional behavior in solution.[1-4] Neither its solid-state nor solution limiting structure is known, though molecular orbital calculations suggest the closo-C_{2v} octadecahedral geometry $[C_{2v}\text{-}(1v^6 2v^4 422)\text{-}\Delta^{18}\text{-}closo]$ to be the most probable (Figure 1). Only one derivative of $B_{11}H_{11}^{2-}$ has been characterized crystallographically. This is the unusual $B_{11}H_9Se_3^{2-}$ species prepared by Todd and co-workers from $B_{11}H_{14}^-$ and polyselenide.[6] The cage geometry was found to be similar to that of the isoelectronic $C_2Me_2B_9H_9$ carborane structure.[7] In both cases, the closo-C_{2v} deltahedral geometry was observed. An analogous geometry was also found in the 11-vertex cage in the metallacarborane $(C_5H_5Co)C_2B_8H_{10}(CoC_2B_8H_{10})$.[8] The lone exception to this structural preference is the $C_2Me_2B_9H_6(OH)_2Br$ structure reported by Scholer where the carborane cage is distorted toward a C_{5v} nido-icosahedral fragment.[9]

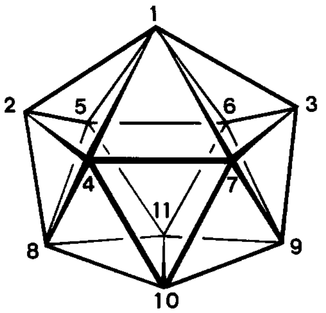

Figure 1. The closo-C_{2v} deltahedron with numbering scheme.

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† National Research Council of Canada. NRC publication No. 20952.

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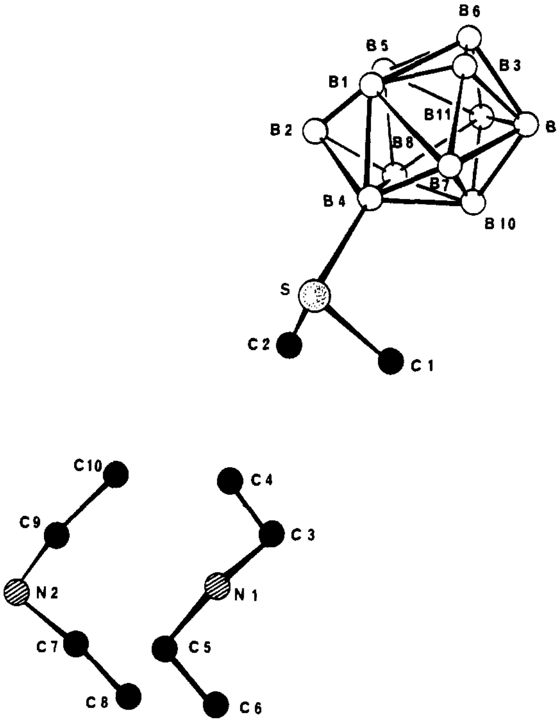

Figure 2. Molecular structure of $(C_2H_5)_4N^+B_{11}H_{10}S(CH_3)_2^-$ (atoms N1 and N2 located on twofold axes).

This was rationalized as a result of electron donation from the oxygen lone pairs into the cage skeletal molecular orbitals, effectively raising the framework electron count from $(n + 1)$ to $(n + 2)$ pairs.[9]

We have been investigating the derivative chemistry of the less symmetrical polyhedral boranes and have recently prepared a dimethyl sulfide derivative of $B_{11}H_{11}^{2-}$ directly from the parent anion.[10] We report here its solid-state structure as determined by X-ray diffraction and its low-temperature boron-11 NMR spectral behavior.

Results and Discussion

The structure of $(C_2H_5)_4N^+B_{11}H_{10}S(CH_3)_2^-$ in the solid state was determined by a single-crystal X-ray diffraction study. The results are shown in Figure 2. The 11-vertex closo geometry is similar to reported cage structures of $B_{11}H_9Se_3^{2-}$, $C_2Me_2B_9H_9$, and $(C_5H_5Co)C_2B_8H_{10}(CoC_2B_8H_{10})$.[6-8] A comparison with the closely related $B_{11}H_9Se_3^{2-}$ structure revealed all the corresponding B–B distances to be within 0.08 Å of each other (esd of 0.02 Å).[6] Thus to date, the closo-C_{2v} geometry is adopted by all the electron-precise 11-vertex polyhedral boranes, carboranes, and metallacarboranes in their crystalline state.

The dimethyl sulfide ligand was found on B(4), one of the vertices with skeletal connectivity five. This would be inconsistent with ground-state molecular orbital results which predicted the five-coordinate (skeletal connectivity four) vertices B(2) and B(3) to be preferred by electrophiles.[11] In view of the solution NMR results to be discussed below, however, crystal-packing forces may dictate the preferred solid-state isomer. Lipscomb and co-workers have estimated the rearrangement barrier in $B_{11}H_{11}^{2-}$ to be only several kilocalories per mole.[3] An analogously small barrier may also be true for $B_{11}H_{10}S(CH_3)_2^-$.

Table I. Atomic Parameters and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms[a]

	x	y	z	B_{eq}, Å^2
S	0.25854 (24)	0.05987 (14)	0.46169 (12)	4.12 (12)
N1	0	0.3541 (6)	$^1/_4$	3.5 (6)
N2	$^1/_2$	0.3497 (6)	$^1/_4$	3.8 (6)
B1	0.2267 (9)	−0.1542 (6)	0.5093 (5)	3.7 (6)
B2	0.3466 (8)	−0.1073 (6)	0.5018 (5)	3.0 (6)
B3	0.1247 (8)	−0.1701 (7)	0.5636 (6)	4.6 (7)
B4	0.2633 (10)	−0.0354 (5)	0.5218 (5)	3.6 (6)
B5	0.3489 (8)	−0.1681 (6)	0.5721 (5)	3.4 (6)
B6	0.2219 (8)	−0.2004 (7)	0.6094 (5)	4.3 (7)
B7	0.1406 (7)	−0.0685 (6)	0.5517 (5)	3.2 (6)
B8	0.3584 (7)	−0.0587 (6)	0.5856 (5)	3.1 (6)
B9	0.1588 (8)	−0.1109 (7)	0.6372 (6)	5.0 (8)
B10	0.2330 (8)	−0.0284 (6)	0.6116 (5)	3.2 (6)
B11	0.2914 (8)	−0.1180 (6)	0.6471 (5)	3.7 (7)
C1	0.1655 (7)	0.1300 (5)	0.4987 (5)	4.6 (6)
C2	0.3752 (7)	0.1124 (6)	0.4833 (5)	5.9 (6)
C3	0.0169 (7)	0.3015 (6)	0.3148 (4)	4.9 (6)
C4	0.1101 (7)	0.2443 (7)	0.3140 (5)	5.8 (6)
C5	0.0944 (7)	0.4091 (5)	0.2359 (5)	4.6 (6)
C6	0.1209 (7)	0.4681 (6)	0.2940 (4)	5.9 (7)
C7	0.5124 (8)	0.4021 (6)	0.3164 (4)	4.8 (6)
C8	0.4209 (6)	0.4631 (6)	0.3321 (6)	7.7 (8)
C9	0.4041 (6)	0.2932 (5)	0.2558 (5)	4.4 (5)
C10	0.4014 (7)	0.2355 (7)	0.3172 (5)	5.9 (7)

[a] Numbers in parentheses in this and subsequent tables refer to esd's of the last digits shown.

Table II. Selected Bond Distances (Å)

S–B4	1.924 (9)	B5–B8	1.797 (14)
S–C1	1.820 (9)	B5–B11	1.812 (14)
S–C2	1.813 (9)	B6–B9	1.757 (16)
B1–B2	1.768 (15)	B7–B9	1.782 (15)
B1–B3	1.722 (15)	B7–B10	1.795 (14)
B1–B4	2.001 (13)	B8–B10	1.804 (15)
B1–B5	2.025 (15)	B8–B11	1.757 (14)
B1–B6	2.048 (14)	B9–B10	1.731 (15)
B1–B7	1.971 (13)	B9–B11	1.772 (15)
B2–B4	1.650 (15)	B10–B11	1.781 (14)
B2–B5	1.662 (14)	N1–C3	1.517 (10)
B2–B8	1.786 (14)	N1–C5	1.560 (10)
B3–B6	1.632 (15)	N2–C7	1.531 (10)
B3–B7	1.677 (15)	N2–C9	1.572 (10)
B3–B9	1.757 (16)	C3–C4	1.545 (14)
B4–B7	1.806 (15)	C5–C6	1.504 (12)
B4–B8	1.791 (15)	C7–C8	1.593 (14)
B4–B10	1.759 (13)	C9–C10	1.498 (14)
B5–B6	1.901 (15)	B6–B11	1.775 (15)

The observed B–S distance of 1.924 (9) Å is similar to those found in dimethyl sulfide derivatives of decaborane and $B_9H_9^{2-}$.[12-15] The N atoms of $(C_2H_5)_4N^+$ were found in special positions (Table I). Important bond distances and angles are presented in Tables II and III.

Proton NMR of the PPN$^+$ (bis(triphenylphosphine)nitrogen(1+)) salt of $B_{11}H_{10}S(CH_3)_2^-$ in $CDCl_3$ exhibited a single methyl signal at 2.40 ppm. This may be indicative of either presence of a single substitution isomer or fluxional behavior in solution. The boron-11 NMR spectrum of this species at room temperature (126.7 MHz) consisted of a singlet at −10.2 ppm and a doublet at −16.9 ppm (J_{BH} = 134 Hz); relative intensities 1:10 (Figure 3). An acetone solution of the salt was cooled down to −80 °C and the temperature dependence of its $^{11}B\{^1H\}$ spectrum observed. The results are shown in Figure 4. Broadening of the major singlet from a half-width of 25 Hz at room temperature to about 200 Hz at −80 °C was observed. These show a linear correlation to changes in solvent

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Table III. Selected Bond Angles (deg)

B4-S-C1	107.1 (5)	B1-B4-B7	62.1 (6)	B6-B9-B11	60.4 (6)
B4-S-C2	102.4 (5)	B2-B4-B8	62.4 (6)	B7-B9-B10	61.4 (6)
C1-S-C2	101.4 (4)	B7-B4-B10	60.4 (6)	B10-B9-B11	61.1 (6)
C3-N1-C5	110.1 (5)	B1-B5-B2	56.3 (6)	B4-B10-B7	61.1 (6)
C7-N2-C9	110.6 (5)	B1-B5-B6	62.8 (5)	B4-B10-B8	60.3 (6)
B2-B1-B4	51.5 (6)	B2-B5-B8	62.0 (6)	B7-B10-B9	60.7 (6)
B2-B1-B5	51.4 (5)	B6-B5-B11	57.0 (6)	B8-B10-B11	58.7 (6)
B3-B1-B7	53.5 (6)	B8-B5-B11	58.3 (6)	B9-B10-B11	60.6 (6)
B4-B1-B7	54.1 (5)	B1-B6-B3	54.4 (6)	B5-B11-B6	64.0 (6)
B5-B1-B6	55.7 (5)	B1-B6-B5	61.6 (6)	B5-B11-B8	60.5 (6)
B1-B2-B4	71.6 (6)	B3-B6-B5	62.3 (7)	B6-B11-B9	59.4 (6)
B1-B2-B5	72.3 (6)	B5-B6-B11	58.9 (6)	B6-B3-B9	62.3 (7)
B4-B2-B8	62.7 (6)	B1-B7-B3	55.6 (6)	B8-B11-B10	61.3 (6)
B5-B2-B8	62.7 (6)	B3-B7-B9	61.0 (6)	B9-B11-B10	58.3 (6)
B1-B3-B6	75.2 (7)	B4-B7-B10	58.5 (5)	N1-C3-C4	116.6 (7)
B1-B3-B7	70.9 (6)	B9-B7-B10	57.9 (6)	N1-C5-C6	115.2 (7)
B7-B3-B9	62.5 (6)	B2-B8-B4	55.0 (5)	N2-C7-C8	114.7 (7)
S-B4-B1	134.1 (6)	B2-B8-B5	55.3 (6)	N2-C9-C10	116.0 (7)
S-B4-B2	116.9 (7)	B4-B8-B10	58.6 (6)	C3-N1-C3′	111.5 (8)
S-B4-B7	113.4 (7)	B5-B8-B11	61.3 (6)	C3-N1-C5	110.1 (5)
S-B4-B8	126.6 (7)	B10-B8-B11	60.0 (6)	C3-N1-C5′	107.5 (5)
S-B4-B10	121.2 (7)	B3-B9-B6	55.4 (6)	C5-N1-C5′	110.3 (7)
B1-B4-B2	57.0 (6)	B3-B9-B7	56.6 (6)	C7-N2-C7′	112.7 (8)
C7-N2-C9	110.6 (5)	C7-N2-C9′	107.1 (5)	C9-N2-C9	108.6 (7)

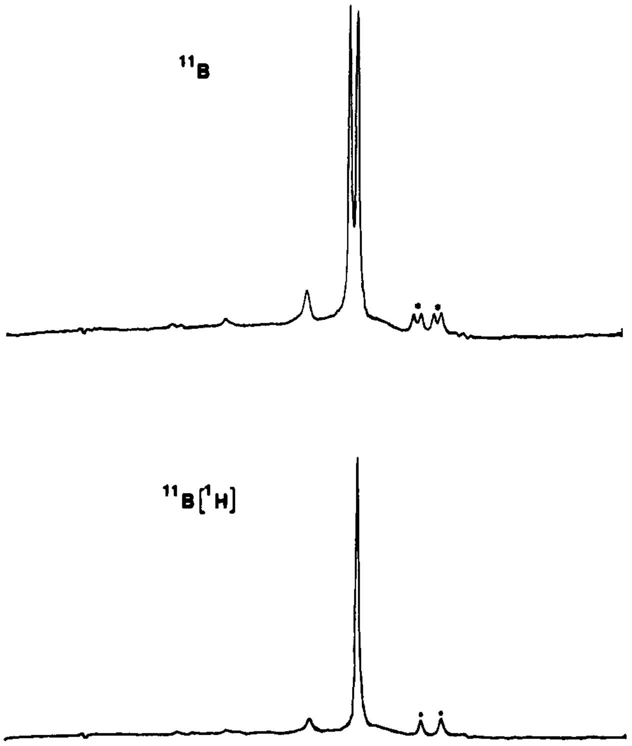

Figure 3. Boron-11 NMR at 126.7 MHz of $PPN^+B_{11}H_{10}S(CH_3)_2^-$ in CD_2Cl_2. Asterisks refer to small amounts of $B_{10}H_9S(CH_3)_2^-$ impurities.

viscosity similar to the previously reported low-temperature spectra of $B_{11}H_{11}^{2-}$.[1] Analogous results were obtained down to about −140 °C in CD_2Cl_2 at 126.7 MHz. These results suggest, though they do not conclusively prove, a degree of fluxionality for $B_{11}H_{10}S(CH_3)_2^-$ comparable to that of the parent $B_{11}H_{11}^{2-}$ species.

Experimental Section

The $(C_2H_5)_4N^+B_{11}H_{10}S(CH_3)_2^-$ salt was prepared as described, and the crystals were grown from warm 18% aqueous acetonitrile.[10] The diffraction intensities of a 0.25 × 0.25 × 0.25 mm crystal were measured at 23 °C with use of graphite-monochromatized Mo Kα radiation generated at 50 kV and 16 mA. The $\theta/2\theta$ scan technique with line profile analysis was used.[16] A total of 5214 measurements

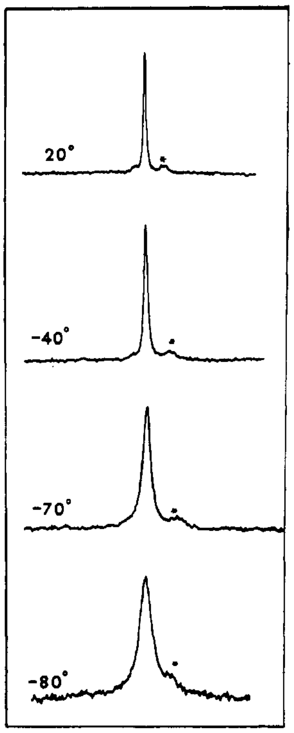

Figure 4. Variable-temperature $^{11}B\{^1H\}$ NMR of $PPN^+B_{11}H_{10}S(CH_3)_2^-$ in acetone-d_6 at 28.7 MHz. Asterisks refer to small amounts of $B_{10}H_9S(CH_3)_2^-$ impurities.

Table IV. Data Collection and Cell Parameters

formula $B_{11}C_{10}H_{36}NS$
space group *Pbcn* orthorhombic
$a = 13.258$ (2) Å
$b = 16.222$ (1) Å
$c = 19.025$ (2) Å
$Z = 8$
$D_{calcd} = 1.043$ g cm^{-3}
$\mu = 0.14$ mm^{-1}
$\lambda = 0.709\,32$ Å (Mo Kα)

cryst dimens: 0.25, 0.25, 0.25 mm
data collected: $0 < 2\theta < 45°$
scan: $\theta/2\theta$
no. of unique reflctns: 2097
no. of data in final refinement: 1173
R_F: 0.082
R_{wF}: 0.055

were made up to 45° in 2θ giving 2697 unique reflections, of which 1173 had net intensities greater than $3\sigma(I)$ based on counting statistics. These were corrected for measured beam polarization.[17] Absorption

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[16] Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.

corrections were not applied since $\mu = 0.14$ mm^{-1}. The cell parameters were obtained by least-squares refinement of the setting angles of 34 reflections with 2θ greater than 35°. Details of the data collection and crystal cell are presented in Table IV.

The structure was solved by using the program MULTAN.[18] The resulting E map revealed all nonhydrogen atoms. The structure was refined with anisotropic thermal parameters and the residual lowered to $R_F = 0.13$. All hydrogens were located in a difference map but were not further refined. Non-hydrogen atoms were refined by block-diagonal least squares with weights based on counting statistics. The scattering curves were taken from the "International Tables for X-ray Crystallography" (1974). Final residuals were $R_F = 0.082$ and $R_{wF} = 0.055$. All calculations were performed by using the NRC PDP8E system of programs.[19] Anisotropic thermal parameters, hydrogen atomic positions, and structure factor tables are included in the supplementary material of this paper.

The boron-11 NMR spectra at 28.7 MHz were obtained with a JEOL FX-90Q spectrometer with D-lock. Chemical shifts were referenced to external $BF_3 \cdot OEt_2$. Perdeuterioacetone was used as a solvent for the low-temperature studies. Probe temperature was monitored with a ^{13}C chemical shift thermometer with use of CCl_4/acetone-d_6.[20] High-field boron-11 spectra were obtained at 126.7 MHz in CD_2Cl_2 solution at the University of California at Los Angeles.

Acknowledgment. We thank the Research Corp. for financial support and the National Science Foundation for an instrument grant toward the purchase of the FT NMR spectrometer. We are also grateful to Paul Behnken of the Department of Chemistry, UCLA, for the high-field boron-11 NMR spectra.

Registry No. $(C_2H_5)_4N^+B_{11}H_{10}S(CH_3)_2^-$, 84642-21-7.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, hydrogen positional parameters, and anisotropic thermal parameters of non-hydrogen atoms (22 pages). Ordering information is given on any current masthead page.

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Oxygen-17 NMR Study of Nickel(II) in Water-Methanol Solvent

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Received May 7, 1982

The effect of inner-sphere methanol on the lability of remaining water molecules in $Ni(H_2O)_n(CH_3OH)_{6-n}^{2+}$ species is of interest in connection with comparisons of various ligands[1] and the general kinetic behavior of solvated ions. Also, the determination of the species present is of essential importance for studied in mixed solvents. In particular Rorabacher[2] and co-workers have done detailed studies of Ni(II) in CH_3OH-H_2O mixtures. Oxygen-17 NMR studies can provide an independent check on species distributions. We have examined a 41.5 wt % CH_3OH solution and find apparently significantly different results on species distribution from those of Rorabacher.

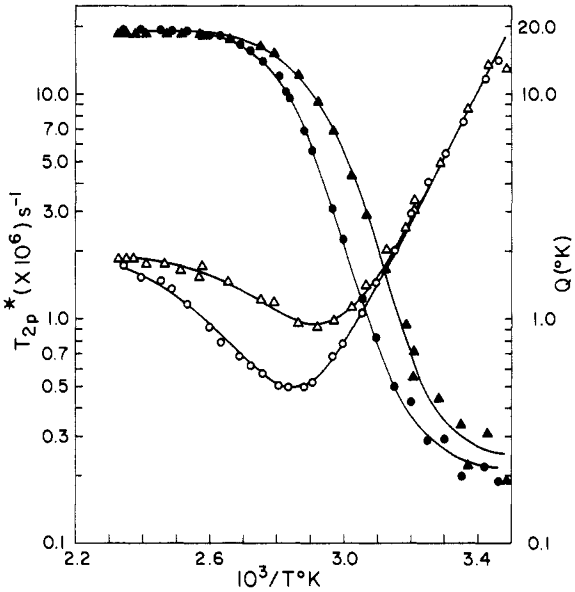

Figure 1. T_{2p}^* and Q vs. $10^3/T$ for aqueous Ni(II)–CH_3OH: (▲, △) Q and T_{2p}^* at 5.75 MHz; (●, ○) Q and T_{2p}^* at 11.5 MHz.

Experimental Section

$Ni(ClO_4)_2 \cdot 6H_2O$ was prepared by recrystallizing the G. F. Smith reagent. It was analyzed by EDTA titration. Water enriched in oxygen-17 at about 4 atom %, originally obtained from Mound Laboratories, Monsanto, Inc., was purified by distillation. The methanol was Baker Analyzed reagent grade as was the perchloric acid used. $Zn(ClO_4)_2 \cdot 6H_2O$ was from G. F. Smith and was used as obtained. The nickel sample was 0.0495 M in Ni(II), 0.01 M in $HClO_4$, 29.22 M in H_2O, and 11.65 M in CH_3OH (41.5% CH_3OH by weight). The zinc blank solution had the same concentrations present. The sample and blank were each placed in 12.5 mm o.d. thick-wall Pyrex glass tubes, which were sealed with a torch.

The NMR equipment and procedures were those described before.[3] The measured line broadenings and shifts of $H_2{}^{17}O$ were converted to T_{2p}^* and Q via the relations

$$1/T_{2p}^* \equiv 2\pi(W_s - W_0)m(H_2O)/m(Ni)$$

$$Q \equiv TSm(H_2O)/m(Ni)$$

where W_s and W_0 are the half-widths (in Hz) at half-maximum absorption for sample and blank and m is the molality. T is in K, and S is the relative frequency shift $(\nu_s - \nu_0)/\nu_0$, where ν_s refers to the nickel sample frequency and ν_0 to the zinc blank frequency. The data were interpreted with Swift and Connick's equations[4] modified to correspond to our use of T_{2p}^* and Q.

Results and Discussion

Figure 1 shows the results of the measurements at two fields. The solid lines are obtained by fitting the data at both fields to the complete Swift-Connick equations with use of a weighted nonlinear least-squares program. The parameters obtained were as follows: k_1(25 °C) = 2.77×10^4 s^{-1}, $\Delta H^* = 12.79$ kcal mol^{-1}, $\Delta S^* = 4.8$ cal mol^{-1} K^{-1}, T_{2M}(144 °C) = 9.5×10^{-6} s, E_a for T_{2M} = 0.21 kcal mol^{-1}, $Q_{lim} = 19.39$ K, $Q_{outer} = 0.24$ K. A field dependence for T_{2M} was not needed to obtain a good fit. These values are computed with use of $\bar{n}$ for H_2O/Ni in $Ni(H_2O)_n(CH_3OH)_{6-n}^{2+}$ equal to 4.91. This value was obtained by assuming the limiting Q_{inner} for a single Ni–OH_2 interaction to be 3.90 K on the basis of empirical observations,[1,3] suggesting that this quantity remains constant, independent of the nature and number of non-water ligands present. Thus $\bar{n} = (19.39 - 0.24)/3.90$. Here Q_{lim} is the high-temperature (fast-exchange) limiting value observed for the solution, Q_{outer} is the outer-sphere value found at low

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