In contrast to the predicted result, the reaction of n-B_9H_{15} with ammonia yields deprotonation[18] followed by fast boron rearrangement to give the known $B_9H_{14}^-$ (a derivative of i-B_9H_{15}) and no bridge cleavage products are isolated. When this reaction is carried out at low temperature and monitored by 70.6-MHz ^{11}B nmr an intermediate is observed (Figure 2a) which may be an isomer of the known $B_9H_{14}^-$. This intermediate appears to be very unstable, since even at low temperatures some of the known $B_9H_{14}^-$ has formed (peaks denoted by ×'s in Figure 2). The spectrum of the intermediate consists of at least six separate resonances suggesting that the symmetry of n-B_9H_{15} is still maintained. Upon further warming of the reaction there appears to be a direct conversion of the intermediate to the known $B_9H_{14}^-$ (Figure 3a) and no other intermediates were observed. The chemical shifts and coupling constants for the intermediate are presented in Table I along with the reported values[18] of n-B_9H_{15}.

Table I

The 70.6-MHz ^{11}B Nmr Spectrum of the Low-Temperature Product of n-B_9H_{15} and NH_3

Resonance[a]	δ, ppm	J, cps
A	−10.4	140
B	−0.6	135
C	10.6	...
D	22.4	~145
E	24.7	~169
F	31.9	145

The 70.6-MHz ^{11}B Nmr Spectrum of n-B_9H_{15}[18]

	δ, ppm	J, cps
B(2)	46.0	157
B(4,9)	32.0	153
B(7,8 or 5,6)	−2.7	148
B(5,6 or 7,8)	−6.6	167
B(3)		
B(1)	−15.9	158

[a] See Figure 2.

The ammonia reaction was repeated using the specifically labeled compound, n-3-$^{10}B^nB_8H_{15}$. Comparison of the ^{11}B nmr spectra of the low-temperature products of the ammonia reaction with the unlabeled and labeled materials (Figure 2a and 2b, respectively) allows the assignment of resonance c as the boron-10 labeled position. This position was formerly the doubly bridged $-BH_2$ position in n-B_9H_{15}. When the ammonia reaction with the labeled material was allowed to go to completion the specifically labeled compound, 4(6,8)-$^{10}B^nB_8H_{14}^-$, was formed. The 70.6-MHz ^{11}B spectrum is presented in Figure 3b. The numbering and structure of $B_9H_{14}^-$ are presented in Figure 4.

Table II

The 70.6-MHz ^{11}B Nmr Spectrum of $B_9H_{14}^-$

	δ, ppm	J, cps
B(5,7,9)	6.62	135
B(4,6,8)	19.7	~145
B(1,2,3)	21.6	150

The reaction of n-B_9H_{15} with sodium amalgam leads to the deprotonation, rearrangement reaction discussed above for ammonia; however, attempts to observe an intermediate in this reaction were unsuccessful.

$$\text{Na-Hg} + n\text{-}B_9H_{15} \longrightarrow Na^+B_9H_{14}^- + {}^1/_2H_2$$

(18) Recent studies have shown that deprotonation is also the initial step in the reaction of tetraborane(10) with ammonia. See H. D. Johnson, II, and S. G. Shore, *J. Amer. Chem. Soc.*, **92**, 7587 (1970).

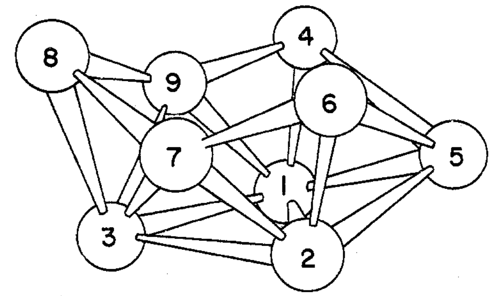

Figure 4.—The structure of $B_9H_{14}^-$.

The only borane detected upon the hydrolysis of n-B_9H_{15} was hexaborane(10), B_6H_{10}. Experimental agreement was found for the equation

$$2n\text{-}B_9H_{15} + 9H_2O \longrightarrow 2B_6H_{10} + 3B_2O_3 + 14H_2$$

Water required for complete hydrolysis: Calcd: 2.8 mmol. Found: 2.3 mmol. Hydrogen evolved in complete hydrolysis: Calcd: 4.3 mmol. Found: 4.1 mmol.

The formation of B_6H_{10} in hydrolysis of n-B_9H_{15} is not surprising since it was shown above that n-B_9H_{15} can undergo cleavage with suitable base to yield octaborane(12) derivatives. Octaborane(12) has been shown to undergo nearly quantitative hydrolysis[8] to hexaborane(10).

Although the ^{11}B nmr of n-B_9H_{15} has been analyzed as resulting from overlapping fragments similar to B_4H_{10} and B_5H_{11},[19] it was felt that if a halogen could be substituted in n-B_9H_{15} it might give complete final proof to the assignment. Substitution of halogens in other boranes has been useful for this purpose.[20] Unfortunately, no halogen derivative could be prepared in this investigation. In all cases where a reaction occurred, complete decomposition of the n-B_9H_{15} structure took place.

Acknowledgment.—Support of this work by the National Science Foundation through Grants GP-4944X and GP-24266X is gratefully appreciated. We also thank Dr. J. E. Dobson for his assistance and comments.

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Nuclear Quadrupole Coupling of Copper Nuclei in Coordination Compounds of Copper(I) with Thiourea and Substituted Thioureas

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Received December 28, 1971

Since the advent of pure nuclear quadrupole resonance (nqr) spectroscopy, resonances for copper nuclei have been published for only two compounds Cu_2O[1] and

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$KCu(CN)_2$.[1,2] Recent crystal structure studies from Amma's laboratory[3-5] indicate that the copper atoms in thiourea and substituted thiourea coordination compounds of copper(I) should be in a sufficiently asymmetric electric field for pure nqr absorption of ^{63}Cu and ^{65}Cu nuclei to be observed. Seven compounds were synthesized and investigated in the 10–50-MHz region, and nqr resonances were measured. The magnitudes of the observed coupling constants can be qualitatively compared.

Experimental Section

Materials.—All ligands used were obtained from either Eastman Kodak Co. or Aldrich Chemical Co. and were used as received. The copper(II) salts used were Baker Analyzed reagents and were used as received.

Preparation of Compounds.—Tris(*N,N'*-dimethylthiourea)-copper(I) chloride was prepared by a method given by Urbanic.[6] The four ethylenethiourea compounds were prepared as suggested by Morgan and Burstall.[7] The two thiourea compounds were prepared by adding a solution of 0.35 mol of thiourea dissolved in a minimum amount of boiling water to a solution of 0.1 mol of the appropriate copper(II) salt dissolved in a minimum amount of boiling water, filtering the resulting mixture while hot to remove sulfur, and cooling in an ice bath to crystallize the desired product. The thiourea compounds were recrystallized from hot water.

Analysis.—The composition of all compounds was ascertained by C–H–N analyses. Experimental and theoretical compositions are given in Table I. All experimental values are averages of duplicate analyses, one by Galbraith Laboratories and one by the Virginia Tech Department of Chemistry Analytical Services.

Table I

Elemental Analysis of Compounds Studied

Compound	Calcd			Found		
	% C	% H	% N	% C	% H	% N
$Cu(tu)_2NO_3$[a]	8.65	2.90	25.14	8.64	2.98	24.51
$Cu_4(tu)_9(NO_3)_4$	9.10	3.06	25.95			
$Cu(tu)_2Br$	8.12	2.73	18.95	7.85	2.74	18.23
$Cu(etu)_2ClO_4$	19.62	3.29	15.25	20.51	3.55	15.88
$[Cu(etu)_3]_2SO_4$	25.86	4.34	20.10	25.53	4.33	19.96
$Cu(etu)_2Cl$	23.76	3.99	18.47	24.44	4.11	19.34
$Cu(etu)_2Br$	20.72	3.48	16.11	21.77	3.69	17.26
$Cu(dmtu)_3Cl$	26.27	5.88	20.42	26.36	6.00	20.26

[a] See note in text regarding this compound.

Powder Patterns.—X-Ray powder patterns were run on the only two synthesized compounds for which single-crystal structures have been determined. The pattern for the thiourea nitrate compound confirms the composition as being $Cu_4(tu)_9(NO_3)_4$. The powder pattern for $Cu(dmtu)_3Cl$ confirms it as being the same compound for which Amma[4] has reported the structure.

Spectrometer.—The nqr spectrometer used was a noise controlled superregenerative spectrometer that has been described elsewhere.[8]

Frequency Measurements.—Frequency measurements were made (1) by suppression of the quench frequency and direct measurement of the CW oscillator frequency with a Hewlett-Packard 5246L Counter and (2) by use of a spectrum analyzer, reference oscillator, and frequency counter.[9] Measurements made by both methods agree within the experimental error of ±0.002 MHz which is determined by the ability to set the oscillator on an absorption peak.

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Results

The observed nqr frequencies for both copper isotopes, when observable are given in Table II. The signal-to-noise (S/N) ratio for the stronger (^{63}Cu) resonance is also given. In addition to the copper resonances ^{79}Br and ^{81}Br resonances were observed at 38.828 and 46.588 MHz, respectively, for $Cu(etu)_2Br$. Also included in the Table II are the observed resonances for $Cu(tu)_2Cl$.

Table II

Observed Nqr Frequencies for Copper(I) Compounds

Compound	Freq, MHz		S/N
	^{63}Cu	^{65}Cu	
$Cu_4(tu)_9(NO_3)_4$[a]	25.088	23.280	5
$Cu(tu)_2Cl$[b]	22.115	20.465	
	19.296	17.856	
$Cu(tu)_2Br$	16.443		3
	16.181		3
$Cu(etu)_2ClO_4$	22.881		3
$[Cu(etu)_4]_2SO_4$	31.562	29.250	20
$Cu(etu)_2Cl$	27.860	25.753	50
$Cu(etu)_2Br$	32.010	29.620	20
$Cu(emtu)_3Cl$	38.804	36.825	5

[a] Key: tu = thiourea, etu = ethylenethiourea, and dmtu = *N,N'*-dimethylthiourea. [b] Resonances observed by G. L. McKown and E. Swiger, private communication.

Discussion

For the discussion which follows the asymmetry parameters for the EFG tensor at the copper nuclei have been assumed to be zero and the quadrupole coupling constant is then double the observed frequency. For the qualitative arguments advanced, this approximation is satisfactory since an asymmetry parameter of $\eta = 0.5$ would only result in a 4% difference in the calculated coupling constant.

A review of the frequencies given in Table II indicates four features that merit discussion. (1) The frequencies are in the vicinity of the reported frequencies for Cu_2O (26.02 MHz)[2] and $KCu(CN)_2$ (33.468 MHz).[3] This indicates that the bonding between the Cu and S atoms in the compounds studied is probably quite covalent, as has been postulated for Cu_2O[10] and $KCu(CN)_2$[11] and as has been shown by the observed Cu–S bond lengths in those compounds studied by single-crystal X-ray diffraction.[3-5]

(2) There are two observed frequencies for the bis(thiourea)copper(I) halides while all other compounds exhibit single resonances. This indicates that the copper atoms in the former compounds occupy at least two crystallographically or chemically inequivalent sites in the unit cell. This has been confirmed by the work of Amma, *et al.*, for $Cu(tu)_2Cl$[3] and $Cu(dmtu)_3Cl$.[4] The occurrence of a single resonance does not eliminate the possibility of multiple sites but if they do exist then their EFG tensor components are very nearly the same.

(3) There is a reversal of the order of the resonance frequencies between the pair $Cu(tu)_2Cl$–$Cu(tu)_2Br$ and the pair $Cu(etu)_2Cl$–$Cu(etu)_2Br$. On the basis of electronegativity considerations the chloride should always have the lower frequency if the Cu–Cl bond is covalent. The Cu–Cl bond length in $Cu(tu)_2Cl$ is of sufficient

(10) H. L. Cox, Jr., *Diss. Abstr.*, **15**, 2254 (1955).

(11) G. L. McKown and J. D. Graybeal, *Inorg. Chem.*, **5**, 1909 (1966).

length to indicate a predominantly ionic bond. For a central atom surrounded symmetrically in a plane by three anions or ligands and having a fourth anion perpendicular to the plane of the ligands an EFG tensor component can pass through zero and exhibit a sign change as the central atom–anion distance changes. In view of this we believe that this apparent abnormality in the order of the frequencies is due to the particular bond lengths that occur in the compounds and does not represent any deviation from normal concepts regarding electronegativity. Consideration of the copper–halogen bond as being predominantly ionic is supported by the low value of the bromine resonances (38.838 and 46.588 MHz) in $Cu(etu)_2Br$. A Townes–Daily calculation using Br_2 as the 100% covalent reference indicates 78% ionic character for the Cu–Br bond.

(4) The observed resonance frequencies for the dimethyl- and ethylenethiourea compounds are in general higher than for the thiourea compounds. The higher frequencies exhibited by the substituted thiourea compounds are probably due to the inductive effect of the substituents on the thiourea ligand. The stability of thiourea resonance forms having a partial negative charge on the sulfur atom is highest for the unsubstituted thiourea; hence it can donate more electron density to the copper atom thereby resulting in a lower p-electron defect and a lower coupling constant.

Acknowledgment.—The authors wish to thank the National Science Foundation for support of this work through Grants GP-9243 and GP-13973. We also thank Dr. G. V. Gibbs and the Virginia Tech Department of Geology for providing necessary X-ray diffraction powder patterns.

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Reorientation of Styrene Groups in Styreneplatinum(II) and -palladium(II) Chlorides

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Received February 15, 1972

In a previous paper[1] we have reported nuclear magnetic resonance studies of mono-styrene derivative complexes of platinum, and the present work is concerned with similar studies of bis-styrene derivative complexes of platinum and palladium. In the bis-styrene complexes, it is known from infrared spectroscopic studies by Chatt[2] and X-ray investigation by Baenziger[3] (Figure 1) that the coordination about the metal atoms is square planar, the terminal and bridge chlorine atoms lie in the plane, and the olefin groups are oriented at right angles to the plane in the trans position in the solid state. Ethylenic proton magnetic resonance spectral lines have been found broader for styreneplatinum(II) chlorides than for styrenepalladium(II) chlorides. The phenomenon is interpreted to show that reorientation of the styrene groups about the coordination bond occurs more slowly in platinum(II) chlorides than in palladium(II) chlorides.

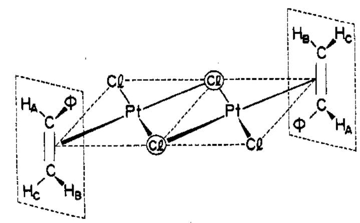

Figure 1.—Structure of styreneplatinum(II) chloride.

Experimental Section

The proton nmr spectra were recorded at 60 MHz on JNM-3H-60 and Varian A-60 spectrometers and calibrated by the usual side-band technique. Styreneplatinum(II) chlorides were stable in acetonitrile solutions for about 1 hr, except 2,3,5,6-tetramethylstyreneplatinum(II) chloride which was stable for a few hours. Styrenepalladium(II) chlorides in chloroform solutions precipitated palladium chloride in 0.5 hr. It was possible, however, to make nmr measurements without any detectable change in chemical shifts and coupling constants before precipitation. Other solvents tried were not suitable for lack of either solubilities or stabilities of the complexes in them. Palladium satellites could not be observed due to the rapid quadrupole relaxation of ^{105}Pd.

p-Methoxy-,[4] *p*-methyl-,[5] *p*-chloro-,[6] and *p*-bromostyrenes[7] were prepared by previously reported methods. 2,3,5,6-Tetramethylstyrene and 2,3,4,5-tetramethylstyrene were supplied by K. Nakamura. All the styrenes were used after redistillation.

Zeise's salt and ethyleneplatinum(II) chlorides were prepared according to the method of MacNevin[8] and of Chatt,[9] respectively. Styrene-, *p*-methoxystyrene-, and *p*-methylstyrene-platinum(II) chlorides were synthesized according to Anderson's method[10] as modified by Orchin.[11]

Di-μ-chloro-dichlorobis(*p*-bromostyrene)diplatinum(II).—*p*-Bromostyrene (0.5 g, 3 mmol) was added to a saturated solution of ethyleneplatinum(II) chloride (0.6 g, 1 mmol) in benzene at room temperature. The solution was concentrated under reduced pressure (15 mm) to give an orange powder. It was washed with petroleum ether (bp 30–70°) and then recrystallized from benzene, yielding orange-yellow crystals. *Anal.* Calcd for $C_{16}H_{14}Cl_4Br_2Pt_2$: C, 21.4; H, 1.6. Found: C, 21.1; H, 1.8.

Di-μ-chloro-dichlorobis(*p*-chlorostyrene)diplatinum(II) was prepared similarly to the *p*-bromostyrene complex. The product is orange-yellow crystals. *Anal.* Calcd for $C_{16}H_{14}Cl_6Pt_2$: C, 23.7; H, 1.7. Found: C, 23.5; H, 1.9.

Di-μ-chloro-dichlorobis(2,3,5,6-tetramethylstyrene)diplatinum(II) monobenzene was prepared similarly to the *p*-bromostyrene complex. The product is orange-yellow crystals. *Anal.* Calcd for $C_{30}H_{38}Cl_4Pt_2$: C, 38.7; H, 4.1. Found: C, 38.4; H, 4.3.

Di-μ-chloro-dichlorobis(2,3,4,5-tetramethylstyrene)diplatinum(II) was prepared similarly to the *p*-bromostyrene complex. The product is orange-yellow crystals. *Anal.* Calcd for $C_{24}H_{32}Cl_4Pt_2$: C, 33.8; H, 3.8. Found: C, 33.5; H, 4.0.

For the preparation of the palladium complexes, the method of Kharasch[12] was followed.

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