

nido-carborane, with the expected cutoff at m/e 202. Its ^{11}B nmr spectrum (with methyl borate as the standard) showed the 1-B as a doublet at δ 67.3 ppm ($J = 188$ cps), the iodinated boron as a doublet at δ 30.9 ppm ($J = 56$ cps, due to one bridge H), and the other two basal boron atoms as an unresolved mound surmounted by sharp peaks, centered at δ 19 ppm, with two-boron intensity. The only possible interpretation was for single iodination at a basal boron adjacent to carbon (3 or 6 position), with the remaining basal boron atoms giving a doublet of doublets superposed upon a doublet of triplets. This is consistent with the better resolved pattern for $\text{ClC}_2\text{B}_4\text{H}_7$.¹

Iodination of the *closo*-Carborane. The reaction of $\text{C}_2\text{B}_4\text{H}_6$ (in excess) with iodine and a trace of Al_2I_6 was just like the iodination of $\text{C}_2\text{B}_4\text{H}_8$ except that the process was very slow at 25° ; it was completed during 24 hr at 75° . Again the major by-products were H_2 and nonvolatile brown material; the yield of the colorless liquid $\text{IC}_2\text{B}_4\text{H}_5$ (vapor pressure 7.9 mm at 0°) represented 20% of the consumed carborane. Its mass spectrum was consistent with a four-boron *closo*-carborane, with the expected cutoff at m/e 200. Its ^{11}B nmr spectrum proved to be simply interpretable: a singlet for 2-BI at δ 50.8 ppm, a doublet for 4-BH at δ 38.2 ppm ($J = 196$ cps), and a doublet twice as intense for 3-BH and 5-BH at δ 34.0 ppm ($J = 189$ cps).

Iodine-Replacement Attempts. Both iodocarboranes proved to be remarkably resistant toward attempts to replace the iodine atom by other atoms or groups. The less stable $\text{IC}_2\text{B}_4\text{H}_7$ (which still required 17 hr at 200° for complete decomposition to H_2 and hydrocarbon-insoluble light-yellow transparent resin and was unaffected by 2537 Å during 24 hr at 20°) reacted with HgCl_2 only when heated but was wholly destroyed during 24 hr at 140° to give 1.0 HCl, 0.40 BCl_3 , and 0.10 H_2 per $\text{IC}_2\text{B}_4\text{H}_7$. The more stable $\text{IC}_2\text{B}_4\text{H}_5$ failed to react with HgCl_2 under similar conditions. Also $\text{Hg}(\text{SCF}_3)_2$ failed to react with $\text{IC}_2\text{B}_4\text{H}_7$ at 20° . An attempt to methylate $\text{IC}_2\text{B}_4\text{H}_7$ by dimethylzinc at 20° showed a fast reaction, leading only to hydrogen and nonvolatiles.

Neither iodocarborane would cleave dimethyl ether at 25° , in contrast to the very interesting cleavage of dimethyl ether by 1- IB_5H_8 at lower temperatures.³

A Quaternary Ammonium Salt. Trimethylamine reacted with 2- $\text{IC}_2\text{B}_4\text{H}_5$ in solution in hexane, precipitating a white solid adduct accurately described by the formula $\text{IC}_2\text{B}_4\text{H}_5 \cdot (\text{CH}_3)_3\text{N}$. It is suggested that this is a quaternary ammonium salt in which one substituent is the 2- $\text{C}_2\text{B}_4\text{H}_5$ group. The instantaneous formation of this salt at 25° would suggest that replacement of iodine from its B-I bond in such carboranes can be done well enough if a base is present, sufficiently strong to displace iodide from the fairly strong B-I bond. However, this would be less likely to succeed in the case of $\text{IC}_2\text{B}_4\text{H}_7$, because this nido structure is relatively sensitive to base action for conversion to resins, whereas $\text{C}_2\text{B}_4\text{H}_6$ is inert toward $(\text{CH}_3)_3\text{N}$.

Registry No. 3- $\text{IC}_2\text{B}_4\text{H}_7$, 34228-48-3; 2- $\text{IC}_2\text{B}_4\text{H}_5$, 38744-24-0; $\text{C}_2\text{B}_4\text{H}_8$, 18972-20-8; $\text{C}_2\text{B}_4\text{H}_6$, 20693-67-8; $\text{IC}_2\text{B}_4\text{H}_5 \cdot (\text{CH}_3)_3\text{N}$, 38744-25-1; iodine, 7553-56-2; trimethylamine, 75-50-3.

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Isomer Characterization of the Ammonia Photoaquation Product of Thiocyanatopentaamminechromium(III)

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The major product of thiocyanatopentaamminechromium(III) photoaquation was earlier reported to be *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$.¹ This configuration was inferred from spectral characteristics, which differed from those of a synthetic sample of *cis*-thiocyanatoaquotetraamminechromium(III). The *trans* isomer was not known at that time. Subsequently, this result became an exception to the pattern emerging for chromium(III) photosubstitutions, since the main photoproducts of other $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$ ions, where $\text{R} = \text{Cl}$,^{2,3} Br ,⁴ RCOO ,⁵ were found, in all cases, to be *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{X}^{2+}$. The exception gave rise to some discussion^{3,6} about possible stereochemical consequences of Adamson's empirical rules for chromium(III) photolysis.^{7,8} The case of $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ has thus assumed a special importance and the recent availability of a reliable synthetic route for the preparation of *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ prompted us to seek a positive characterization of the isomer form of the photo-produced thiocyanatoaquotetraamminechromium(III) complex. Through accurate spectral and kinetic measurements we have obtained definitive evidence that, contrary to the previous assignment, the photoproduct consists of at least 95% *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$.

$[\text{Cr}(\text{NH}_3)_5(\text{NCS})](\text{ClO}_4)_2$ and *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ were prepared as described,¹ the latter complex being obtainable only in solution. *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ was precipitated as the perchlorate salt after controlled acid hydrolysis, in the dark, of *trans*- $\text{Cr}(\text{NH}_3)_4(\text{NCS})\text{Cl}^+$, which, in turn, was synthesized⁹ by thiocyanate anation of *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$.¹⁰ *Anal.* Calcd for $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})](\text{ClO}_4)_2$: Cr, 13.16; NCS, 14.70; N, 17.72. Found: Cr, 12.9; NCS, 14.4; N, 17.4. The maxima of the ligand field absorption bands, L_1 and L_2 ,⁸ for the two aquothiocyanato isomers are reported in Table I along with the crossing points with the spectrum of thiocyanatopentaamminechromium(III). The extinction coefficients of the *cis* isomer are found to be slightly higher than previously reported.¹ The absorption spectra of both isomers in acid solution remain unchanged over a period of at least 12 hr.

Aqueous solutions of *ca.* 10^{-2} M thiocyanatopentaamminechromium(III) in 5×10^{-3} M HClO_4 were irradiated at room temperature in 1-cm cells with 480-nm light (selected by means of a Baird-Atomic interference filter 11-94-5). The photoproduct has a much lower absorption than the starting

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Table I. Spectral Features and Thiocyanate Aquation Rate Constants at 70° for $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ Ions

Species	λ , nm (ϵ)		Isosbestic points, ^a nm	$10^6 k$, ^d sec ⁻¹
	L_1	L_2		
Photoproduct	497 (74)	373 (48)	505, 423, 372 ^b	17.5 ± 0.9
Cis	497 (70 \pm 2)	372 (47 \pm 2)	506, 423, 373 ^c	18.0 ± 0.8
Trans	510 (50.0)	371 (45.7)	523, 418, 383 ^c	3.68 ± 0.15

^a With $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$. ^b Experimental. ^c Calculated. ^d In 0.1 M HClO_4 , $\mu = 2$, adjusted with NaClO_4 .

complex at this wavelength (see Figure 1) so that inner-filter effects and secondary photolysis are minimal. Also, thermal processes may be ignored under the above conditions.¹ The energy absorbed was determined by continuous differential measurements, using a thermopile. A typical experiment is illustrated in Figure 1. A 3-ml sample of 8.1×10^{-3} M solution was irradiated for successive 4- or 6-min periods. The average intensity absorbed was around 9×10^{-7} einstein min^{-1} . After each period the optical density of the photolyzed solution was measured against that of an identical dark sample, using the expanded scale of a Shimadzu MPS 50 L recording spectrophotometer. The differential spectra show three sharp isosbestic points which are present up to at least 25% aquation. The known absorption spectra (see Table I) and quantum yields, $\phi_{\text{NH}_3} = 0.42$ and $\phi_{\text{NCS}} = 0.021$ (4.5% $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ is present among the photoproducts) allow the absorption spectrum of the main photoaquation product to be calculated. Again, some differences from previous data¹ are observed. Figure 1 also shows the spectral changes expected for 25% aquation assuming that either *cis*- or *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ is the ammonia aquation product. Comparison with the experimental curves shows that most, if not all, of the ammonia photoaquation product appears now to be the *cis* isomer.

It seems appropriate to look for the possible reasons which previously led to the misassignment of the configuration. In the first place, as already predicted,¹ by analogy with $\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{NCS})^{2+}$ ions, the spectra of the two tetraammine isomers do not, in fact, show differences as marked as those generally observed between other *cis*- and *trans*-diacidotetraamminechromium(III) complexes. That is, *trans*-diacidotetraamminechromium(III) complexes generally have a much lower extinction coefficient and a higher degree of splitting of the L_1 band, relative to the corresponding *cis* species than does *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$. Second, the spectrum of one of the isomers was unknown and the *trans* configuration was deduced from relatively small—although predicted—spectral differences between the *cis* form and the photoproduct present in solution after precipitation of the starting complex. Small amounts of other chromium(III) species, sufficient to modify the spectral features, may have remained in solution.

Since the differences in absorption between *cis* and *trans* isomers are not as drastic as for $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$,³ the spectral arguments might not be regarded as compelling. Therefore, independent evidence was sought by comparison of the rate constants for thiocyanate thermal aquation of the two synthetic isomers with that of the photoproduct. Solutions of the latter were obtained by precipitating excess $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ from photolyzed samples with an appropriate amount of NaClO_4 . The presence of free NCS^- , due to aquation of unprecipitated parent complex, was taken into account by treating an identical dark sample in the same way.

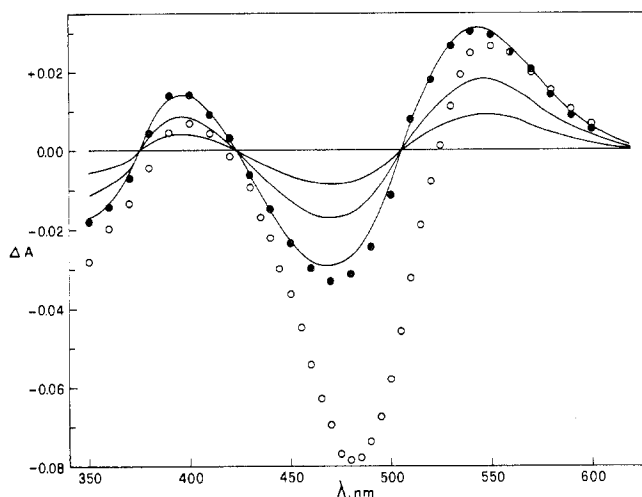


Figure 1. Differential spectra during photolysis of aqueous thiocyanatopentaamminechromium(III) at 480 nm. Reading downward at 480 nm, the curves correspond to 7.3, 14.7, and 25.3% of reaction. Circles represent spectral variation calculated for 25.3% conversion to *cis*- (●) and *trans*- (○) thiocyanatoaquotetraamminechromium(III).

The kinetic measurements at 70° were carried out at least in duplicate using solutions *ca.* 2×10^{-3} M in complex in 0.1 M HClO_4 (of ionic strength 2 M, with sodium perchlorate, necessary for the above precipitation and for the ion-exchange separation of the *cis*-aquothiocyanato ion).¹ Released thiocyanate was determined spectrophotometrically with iron(III) reagent.¹ In all cases the aquation reactions follow first-order kinetics up to at least 50%. The rate constants are reported in Table I. The values for *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ and for the photoproduct coincide within experimental error, while the rate for the *trans* isomer is slower by a factor of 5. As has already been pointed out,¹ complications due to thermal isomerization either of the photolysis product or of the synthetic samples are highly improbable, since retention of configuration is usually observed in thermal substitutions of chromium(III) complexes.^{11,12} Literature data¹² on the thermal aquation of the acido group, X, in other *cis*- and *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{X}^{2+}$ (X = Cl) or $\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{X}^{2+}$ (X = NCS, Cl, Br) ions, show that, as in the present case, the rate constants for the *trans* complexes are always lower by an order of magnitude than for the *cis* isomers. The presence of 0.05 M SO_4^{2-} increases the first-order rate constants of the *cis* ion and of the photoproduct by a factor of *ca.* 2 whereas it causes a deviation from first-order kinetics in the case of the *trans*. This observation provides additional evidence for a *cis* photoproduct.

Returning to the discussion of ref 3 and 6, the knowledge that the configuration of the photoproduct is definitely *cis* (instead of *trans*) makes the photoaquation stereochemistry of the $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$ series uniform. For these systems the situation is that the empirical rules correctly predict mainly NH_3 photoaquation, *i.e.*, that the ligand released is of the same type as that of greater field strength on the weakest average-field axis. A necessary condition to the interpretation of the stereospecificity of the photoreaction is that the *particular* NH_3 ligand photoaquated be known. Such information is not available.

However, a recent inspection of the photochemical behavior of some mixed-ligand Cr(III) ions has shown that stereomobility is usually involved in chromium(III) photo-

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aquation,⁶ while retention of configuration generally occurs in thermal paths.^{11,12} Thus, *trans*-Cr(en)₂Cl₂⁺ photoaquates chloride, yet at least 70% of the product is *cis*-Cr(en)₂(H₂O)Cl₂⁺,¹³ and the photoproducts of several *trans*-Cr(NH₃)₄XY ions, where the acido groups X and/or Y are the only ones to be aquated, are exclusively *cis*.¹⁴ Furthermore, stereomobility may well be a necessary condition for photosubstitution to occur; *trans*-Cr(cyclam)Cl₂⁺, in which rigidity is imposed by the cyclam¹⁵ ring is, in fact, photoinert.¹⁶ These findings suggest that the NH₃ photoreleased in thiocyanatopentamminechromium(III), and in the other Cr(NH₃)₅X²⁺ systems, is indeed most probably the one in *trans* position to the acido group. The present results eliminate an apparent exception and it now appears that a uniform photoaquation mechanism applies to chromium(III) amines and, moreover, one which requires stereomobility, that is, *trans* → *cis* isomerization, for its occurrence.

Registry No. [Cr(NH₃)₅(NCS)](ClO₄)₂, 22478-28-0; *cis*-Cr(NH₃)₄(H₂O)(NCS)²⁺, 38781-21-4; *trans*-[Cr(NH₃)₄(H₂O)(NCS)](ClO₄)₂, 38781-22-5.

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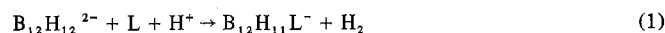
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Direct Synthesis of Dialkyl Sulfide Derivatives of Dodecahydrododecaborate(2-), B₁₂H₁₂²⁻

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A number of Lewis bases react with the B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻ ions under acidic conditions, and the reaction can formally be treated as a displacement of a hydride ion by the base, as shown in eq 1. A neutral base reduces the charge



of the polyhedral system by one unit; an anion will leave it intact. The investigators who first explored these reactions^{1,2} found that water inhibited and high proton concentration promoted the substitution. Some protonated form of the polyhedral ions was assumed to be a key reaction intermediate in these reactions.¹ We have been interested for some time in the effects of ionic charge on the chemical properties of functional groups attached to the polyhedral cage. Several types of substituents capable of reducing the charge on the polyhedron are known, but many of them are quite reactive and interfere with subsequent substitutions at other boron sites. Since we have found the -SR₂⁺ group to

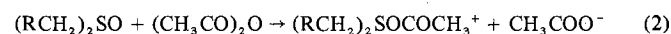
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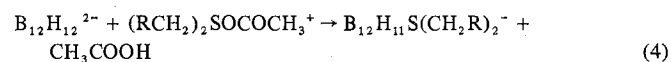
be the most satisfactory because of its inertness, we decided to look for high-yield syntheses of dialkyl sulfide derivatives of polyhedral boranes. A satisfactory method has been published for the synthesis of dimethyl sulfide derivatives of the B₁₀H₁₀²⁻ ion.³ However, the simple one-step reaction with methyl sulfoxide fails to proceed under similar conditions with the B₁₂H₁₂²⁻ ion.³ Multiplicity of steps and low overall yields make the three methods reported for the synthesis of B₁₂H₁₁SR₂⁻ derivatives quite unsatisfactory. The oldest method starts with diborane and an alkyl sulfide as the base in the cage-condensation reaction.⁴ Alkylation of B₁₂H₁₁SH²⁻, which is made from B₁₂H₁₂²⁻ and H₂S,⁵ or of B₁₂H₁₁SR²⁻, which is made from B₁₂H₁₂²⁻ and alkyl disulfides,⁵ will also yield the desired products.

Results and Discussion

The reaction of B₁₀H₁₀²⁻ with aqueous acidic methyl sulfoxide results in the elimination of water and the formation of a boron-sulfur bond, in contrast with similar reactions involving sulfones where the sequence of bonds is boron-oxygen-sulfur.¹⁻³ The formation of the dialkyl sulfides was attributed to an electrophilic attack on the polyhedral ion by the R₂SOH⁺ species. In support of this mechanism was cited the failure of the B₁₂H₁₂²⁻ ion to react.³ Believing the proposed mechanism to be essentially correct we decided to look for conditions which would remove water from the reaction mixture and replace the R₂SOH⁺ intermediate with a more reactive species. Acylation of methyl sulfoxide yields an ion of the type R₂SOCOR⁺ which is reactive enough, even under moderate conditions, to produce alkyl sulfide derivatives of B₁₂H₁₂²⁻ in a one-step reaction. The prerequisite reaction conditions are those first reported in 1910 by Pummerer,⁶ who found that sulfoxides containing at least one methyl or methylene group adjacent to sulfur react with acetic anhydride to give α-acetoxy sulfides. The mechanism of the Pummerer reaction has been investigated by a number of workers, and it would appear that two distinct steps are involved: the formation of the acetoxy-sulfonium ion and its subsequent rearrangement to the acetoxy sulfide.⁷



In the presence of the polyhedral ions the Pummerer reaction is inhibited, and instead of the α-acetoxy sulfide the principal products are alkyl sulfide derivatives of the polyhedral boranes. The results suggest that an electrophilic attack on the polyhedral ion followed by elimination of acetic acid occurs before the acetoxy-sulfonium has an opportunity to rearrange (eq 4). If an excess of sulfoxide and



anhydride is used and more time is allowed, the mono-substituted ion reacts with another acetoxy-sulfonium and the neutral B₁₂H₁₀[S(CH₂R)₂]₂ is the predominant product. Through a suitable choice of temperatures and

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