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Acid-assisted Oxidation of Decachlorodecaborate 2(–): Synthesis and Characterization of a Ten-vertex Polyhedral Borane Radical

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In the presence of Lewis acids, lead tetraacetate rapidly oxidized decachlorodecaborate (2–), $B_{10}Cl_{10}^{2-}$*, to the blue-violet radical anion* $B_{10}Cl_{10}^{-}$*. No reaction was observed in the absence of Lewis acids or trifluoroacetic acid. The isolated* $B_{10}Cl_{10}^{-}$ *radical is quite stable and its IR, electronic, and ESR spectra are reported. Chemically it behaves as a superior oxidizing agent and competitive reactions indicated the following order of oxidizing power;* $B_{10}Cl_{10}^{-} > B_9I_9^{-} > B_9Br_9^{-} > B_9Cl_9^{-}$*. The possible role of the acids in the synthesis of* $B_{10}Cl_{10}^{-}$ *is discussed.*

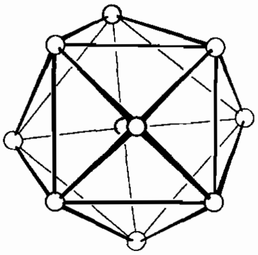

Fig. 1. The Ten-vertex Polyhedron of $B_{10}H_{10}^{2-}$ and $B_{10}Cl_{10}^{2-}$.

Introduction

The ten-vertex polyhedral borane $B_{10}H_{10}^{2-}$ (Fig. 1) is one of the most studied boron hydrides and has often been compared to the organic aromatics [1]. The robustness of the ten-boron cage is substantiated by the large variety of electrophilic and nucleophilic substitution reactions that can be carried out on it. Generally the closed-shell polyhedral boranes have relatively high resistance towards redox reactions. This is especially true of the very stable perhalogenated derivatives of $B_{10}H_{10}^{2-}$. For example, $B_{10}Cl_{10}^{2-}$ is not oxidized up to +1.1 volts (sce) in aqueous solutions while the parent $B_{10}H_{10}^{2-}$ undergoes oxidative coupling reactions at 0.85 volt [2, 3].

We have recently reported the existence of the three oxidation states of nine-boron halide clusters: $B_9X_9^{2-} \rightleftharpoons B_9X_9^{-} \rightleftharpoons B_9X_9^{0}$ (X = Cl, Br, I) using both chemical and electrochemical techniques [4, 5]. It can be expected that similar oxidation of a ten-vertex boron halide cluster may prove considerably more difficult due to the higher oxidative stability. We have attempted chemical oxidations of the $B_{10}Cl_{10}^{2-}$ species with the objective of isolating the $B_{10}Cl_{10}^{-}$ radical and to investigate its spectral and chemical properties. Previous reports of B_{10}-radicals include the transient $B_{10}H_{10}^{-}$ species whose 'weak' esr spectrum was reported by Middaugh and Farha [6]. Kaczmarczyk also reported the esr spectra of dark violet radicals formed by the oxidation of $K_2B_{10}H_{10}$ with $FeCl_3$ or $CuCl_2$ in ethereal solutions [7]. None of the proposed species, however, has been isolated or characterized and their identities remain suspect.

Results and Discussion

Reaction of excess thallic trifluoroacetate with $(n\text{-}Bu_4N)_2B_{10}Cl_{10}$ in methylene chloride solution yielded a red–purple suspension from which a black solid can be isolated. Infra-red spectral analysis of the solid indicated new bands in the cage vibration region at 1075 and 960 cm^{-1} in addition to the $B_{10}Cl_{10}^{2-}$ absorptions. Elemental analysis also confirmed the presence of unoxidized $B_{10}Cl_{10}^{2-}$ in the product. Attempts at isolating the pure oxidation product were unsuccessful.

When lead tetraacetate was used as the oxidant no reaction at all was observed with $(n\text{-}Bu_4N)_2B_{10}Cl_{10}$ in CH_2Cl_2 solution. It was noticed that addition of excess amounts of Lewis acids such as BF_3, $AlCl_3$, and especially $SnCl_4$ resulted in immediate darkening of the reaction mixture to a blue–violet coloration. Work-up and recrystallization yielded a black, irridescent solid that analyzed as $(n\text{-}Bu_4N)B_{10}Cl_{10}$. Yields are typically between 50–70%. It was also found that addition of trifluoroacetic acid in lieu of the

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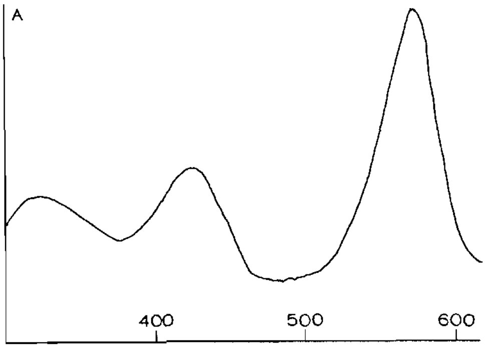

Fig. 2. Electronic Spectrum of $(n\text{-}Bu_4N)B_{10}Cl_{10}$ in CH_2Cl_2.

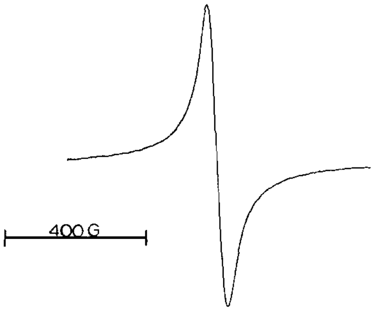

Fig. 3. ESR of $(n\text{-}Bu_4N)B_{10}Cl_{10}$ as a frozen solution in $SOCl_2$.

Lewis acids also resulted in facile formation of the anionic radical.

Solutions of $B_{10}Cl_{10}^{-}$ in nonpolar solvents like CH_2Cl_2 are dichroic transmitting blue light and reflecting violet light. Its electronic spectrum included absorption maxima at 322 (ϵ 3,400), 424 (ϵ 4,200), and 574 (ϵ 9,800) nm (Fig. 2). An infrared spectrum of the solid showed strong, broad bands at 1075 and 960 cm^{-1} in the cage vibration region similar to the spectra of the $B_9X_9^{-}$ radicals [4].

The ^{11}B NMR of $B_{10}Cl_{10}^{-}$ in CH_2Cl_2 or $SOCl_2$ solutions displayed only a broad, featureless signal centered at about 0 ppm with a half-width of approximately 80 ppm. This is consistent with NMR signal broadening due to the paramagnetic anion. Room temperature ESR spectrum of a polycrystalline sample of $(n\text{-}Bu_4N)B_{10}Cl_{10}$ displayed an extremely broad signal with a peak to peak width (ΔH_{pp}) of over 800 G. Upon cooling to 77 K, a slightly better resolved signal was observed at $g = 2.04$ ($\Delta H_{pp} = 330$ G). Room temperature ESR of a solution of the anion in $SOCl_2$ exhibited only a very weak signal. Cooling to 77 K produced a strong absorption at $g = 2.04$ ($\Delta H_{pp} = 55$ G) (Fig. 3). This can be compared with the frozen solution spectrum of $(n\text{-}Bu_4N)B_9Cl_9$ in $SOCl_2$ with a g-value of 2.03 ($\Delta H_{pp} = 50$ G). In all these cases, only a single resonance is observed with no evidence of fine structure. This is not unexpected with the presence of the quadrupolar nuclei ^{10}B ($I = 3$) and ^{11}B ($I = 3/2$) in the ten-vertex polyhedron and ^{35}Cl ($I = 3/2$) and ^{37}Cl ($I = 3/2$) as the exopolyhedral substituents.

As solids, salts of $B_{10}Cl_{10}^{-}$ with large cations are stable indefinitely in dry air. Solutions in CH_2Cl_2 and $SOCl_2$ do not decompose when kept under dry nitrogen atmosphere. Addition of donor solvents such as THF, dimethoxyethane, or alcohols rapidly discharged the deep blue-violet color of $B_{10}Cl_{10}^{-}$ and regenerated the $B_{10}Cl_{10}^{2-}$ species.

As expected, $B_{10}Cl_{10}^{-}$ is a superior oxidizing agent chemically and can be easily assayed photometrically by titration with $(n\text{-}Bu_4N)I$ in CH_2Cl_2 solution:

$$2B_{10}Cl_{10}^{-} + 2\ I^{-} \rightarrow 2B_{10}Cl_{10}^{2-} + I_2$$

Competitive reactions with the $B_9X_9^{-}$ radicals clearly demonstrated that $B_{10}Cl_{10}^{-}$ is capable of oxidizing all the $B_9X_9^{2-}$ and $B_9X_9^{-}$ anions to the neutral B_9X_9 clusters.

$$B_{10}Cl_{10}^{-} + B_9X_9^{2-} \rightarrow B_{10}Cl_{10}^{2-} + B_9X_9^{-}$$

$$B_{10}Cl_{10}^{-} + B_9X_9^{-} \rightarrow B_{10}Cl_{10}^{2-} + B_9X_9$$

$$(X = Cl, Br, I)$$

The oxidative power of these boron halide radicals can be ranked in the order: $B_{10}Cl_{10}^{-} > B_9I_9^{-} > B_9Br_9^{-} > B_9Cl_9^{-}$.

There are at least two possible roles for the Lewis acids in the oxidative synthesis of $B_{10}Cl_{10}^{-}$ reported here. One is the activation of the Pb(IV) center to give a stronger electrophile in the manner of a Friedel-Crafts catalyst [8].

$$Pb(OAc)_4 + Acid \rightleftharpoons Pb(OAc)_3^{+} + Acid(OAc)^{-}$$

It is well known that $SnCl_4$, for example, can form adducts with donor ligands to give species like $SnCl_4 \cdot L$ and $SnCl_4 \cdot 2L$ [9]. A second role for the Lewis acids may be to polarize the delocalized electron density in the $B_{10}Cl_{10}^{2-}$ cage, facilitating electron removal by the oxidant. For example:

$$SnCl_4 + B_{10}Cl_{10}^{2-} \rightleftharpoons Cl_4Sn^{-}\text{–}Cl\text{–}B_{10}Cl_9^{-}$$

We have not been able to obtain spectroscopic evidence for any adduct formation between $B_{10}Cl_{10}^{2-}$ and Lewis acids but cannot rule out the possibility of weak adducting or simple ion-pairing as being sufficient to assist in the oxidation process. That such an activation is *not* required for the successful completion of the oxidation process can be illustrated by the following experiment. We found that *in situ* preparation of $Pb(TFA)_4$ from $Pb(OAc)_4$

and excess trifluoroacetic acid produced a hydroscopic solid that successfully oxidized $B_{10}Cl_{10}^{2-}$ without further need for Lewis acids. We therefore favor at this time the potentiation of the Pb(IV) oxidant by the Lewis acids and trifluoroacetic acid as the major reason for the successful oxidation of $B_{10}Cl_{10}^{2-}$. Literature contains many examples of the superior electrophilicity of thallic and plumbic trifluoroacetates compared to acetates in metallation reactions on organic aromatic systems [10, 11].

Further oxidation of the $B_{10}Cl_{10}^{\overset{-}{\cdot}}$ radical to give the known neutral $B_{10}Cl_{10}$ cluster remains to be achieved using chemical oxidants. By analogy to the $B_9X_9^{\overset{-}{\cdot}}$ oxidations [5], we would expect at least another +0.5 volt in electrode potential to effect $B_{10}Cl_{10}$ formation, and a much more powerful oxidant than Pb(IV) will be required to accomplish this conversion.

Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen in Schlenk glassware. Methylene chloride was distilled under N_2 from CaH_2. (n-Bu_4N)Cl, (n-Bu_4N)I, $SOCl_2$, SO_2Cl_2, $SnCl_4$, TFA, and N-Chlorosuccinimide were obtained from Aldrich Chem. Co. (n-$Bu_4N)_2B_{10}H_{10}$ was prepared from literature procedure [12]. Lead tetraacetate was prepared according to Fieser and Fieser [13].

IR spectra were obtained as Nujol mulls or KBr pellets on a Perkin Elmer 337 spectrometer. ^{11}B NMR was recorded on a JEOL FX-90Q spectrometer with external $BF_3 \cdot OEt_2$ reference and D-lock. Electronic spectra were taken on a Cary 14 spectrophotometer. ESR data were collected on a Varian E-4 spectrometer at room temperature and liquid nitrogen temperature.

Preparation of (n-Bu₄N)₂B₁₀Cl₁₀

An amount of 4.45 g (7.43 mmol) of (n-$Bu_4N)_2B_{10}H_{10}$ was stirred with 1.0 g (74.3 mmol) of N-chlorosuccinimide in 100 ml of CH_2Cl_2. After 24 hrs, the suspension was evaporated to dryness and washed with methanol to give 5.1 g of crude product. To ensure complete chlorination, 5 ml of SO_2Cl_2 was added to the solid in 50 ml of CH_2Cl_2. After stirring for 4 hrs, the mixture was evaporated to dryness, washed with methanol and recrystallized from warm acetonitrile methanol to give 4.24 g (60%) of pure (n-$Bu_4N)_2B_{10}Cl_{10}$.

Preparation of (n-Bu₄N)B₁₀Cl₁₀

(A) An amount of 2.4 g (2.5 mmol) of (n-$Bu_4N)_2B_{10}Cl_{10}$ and 2.4 g (5.5 mmol) of $Pb(OAc)_4$ were stirred in 75 ml of CH_2Cl_2. 3.0 ml of $SnCl_4$ was added and the resulting dark suspension stirred for two hrs. After filtration through Celite, the filtrate was evaporated to dryness and washed with 2 X 20 ml of benzene. The residue was redissolved in 40 ml of CH_2Cl_2 and filtered. Slow concentration of the filtrate to about 15 ml gave a crystalline precipitate. Filtration and drying yielded 1.1 g (65%) of black, crystalline solid. *Anal.* for $C_{16}H_{36}NB_{10}Cl_{10}$. Calc.: %C, 27.27; H, 5.11; N, 1.99; B, 15.34; Cl, 50.30. Found: %C, 26.97; H, 5.40; N, 2.1; B, 15.05; Cl, 49.96. (Elemental analyses were by Schwartzkopf Analytical Co., Woodside, New York.)

(B) An amount of 400 mg of $Pb(OAc)_4$ was dissolved in 5 ml of TFA and the clear solution evaporated to dryness to give a white, hydroscopic solid. A CH_2Cl_2 solution of 400 mg of (n-$Bu_4N)_2B_{10}$-Cl_{10} was added via a syringe. The resulting dark mixture was stirred for 4 hrs and filtered through Celite. The filtrate was evaporated to dryness and washed with 20 ml of benzene. Recrystallization of the dark residue from CH_2Cl_2 gave 100 mg (30%) of (n-Bu_4N)-$B_{10}Cl_{10}$.

Competitive Oxidations with $B_9X_9^{\overset{-}{\cdot}}$

Stoichiometric amounts of (n-$Bu_4N)B_{10}Cl_{10}$ and (n-$Bu_4N)B_9X_9$ [4] were mixed in CH_2Cl_2. After the dark–blue color of $B_{10}Cl_{10}^{\overset{-}{\cdot}}$ was discharged, the solvent was removed and the residue extracted with n-hexane for X = Cl, Br and CCl_4 for X = I. Solvent removal from these extracts yielded the corresponding B_9X_9 clusters identifiable by spectral means.

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