CATIONIC COMPLEXES

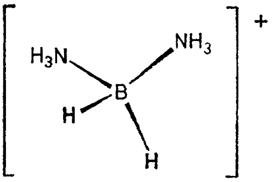
E. L. Muetterties

Central Research Department,
E. I. du Pont de Nemours and Company, Wilmington 98, Delaware, U.S.A.

Cationic complexes of metals and non-metals in the d^0 or d^{10} configuration are an incompletely characterized group. Definitive data on structure, stability, and reaction mechanism are few in number despite the fact that one of the first examples of a stable cationic complex, the tris-(acetylacetonato)silicon(IV) cation, appeared in 1903[1]. In recent years, we have explored the synthesis of cationic complexes and have attempted detailed characterization of several new cations[2–5]. The status of our investigation is reviewed in this paper.

Boronium ions[2,12]

In the classic work by Parry and co-workers[6], the "diammoniate of diborane" was structurally resolved as a salt in which the cation is 1:



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Since that time a number of analogues of this highly reactive cation have been prepared[2, 7–10] and some of these have fairly good stability. In particular, we have found several general synthetic procedures for derivatives of 1 in which the ammonia ligands are replaced by dialkylsulphides and by tertiary amine, phosphine, and arsine groups. These are summarized in the following equations where L is a general notation for the Lewis base.

$$LBH_3 + LH^+X^- \longrightarrow H_2BL_2^+X^- + H_2 \qquad (1)$$

$$2LBH_3 + 11/2B_2H_6 \longrightarrow H_2BL_2^+B_{12}H_{11}L^- + 10H_2 \qquad (2)$$

$$H_2BL_2^+ + 2L' \longrightarrow H_2BL_2'^+ + 2L \qquad (3)$$

All of these cations were rigorously established as structural analogues of 1 by i.r. and n.m.r. data but no structural parameters have been determined. Nordman and Peters[11] have determined the parameters for 1 from an X-ray diffraction study of the chloride salt. The chloride salts of the $H_2B(NR_3)_2^+$ cations are strong electrolytes, and the hydroxides exhibit typical strong base behaviour.

The bisamine cations, $H_2B(NR_3)_2^+$, have rather remarkable chemical stability. Concentrated sulphuric, hydrochloric, and nitric acids and strong alkali are without effect on the bisamine cations. Even aqua regia does not degrade the cations at 100° although one BH hydrogen atom is displaced by chlorine to give $HClBL_2^+$. No oxidation of the cations occurs with reagents like gold(III) salts and 30 per cent hydrogen peroxide at temperatures up to 100°. The amine cations also resist electrophilic species such as iodine and Friedel-Crafts reagents.

Molecular models show the boron atom in any of the bisamine cations to be effectively shielded by the ligands; any transition state or reaction intermediate in which there is a five-coordinate boron atom should be a very high energy state. Thus, spatial factors must account for much of the chemical stability of these boronium ions. The positive charge is probably transferred to some extent to the BH hydrogen atoms thus reducing their hydridic character and raising the barrier to attack of the BH bonds by hydronium ion. Reluctance of the cations to undergo electrophilic substitution at the BH bonds reflects the coulombic repulsion inherent in a cation-electrophile combination and also the sterically congested innards of the cation.

The trimethylphosphine derivative, $H_2B[P(CH_3)_3]_2^+$, like the bisamine cations, is resistant to mineral acids; however, it succumbs to warm aqueous base. Degradation of the trimethylarsine cation is moderately fast in hot water, and the sulphide cation is rapidly hydrolysed in cold water. We suggest that attack on $H_2B(PR_3)_2^+$ by hydroxyl ion initiates at the positively charged and sterically unhindered phosphorus atom. A similar reaction course may prevail in the hydrolyses of the arsine and sulphide complexes, but in these cations the boron atom is not as effectively shielded by the ligands and the arsine and sulphide ligands are quite susceptible to dissociation (*vide infra*).

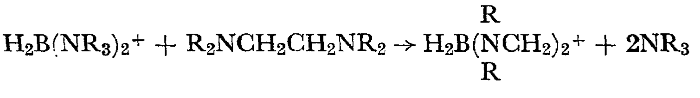
Thermal stability of the bisamine cations, $H_2B(NR_3)_2^+$, is a function of the associated anion. Most of the salts in which the anion is large undergo no decomposition below ~180°. If the anion is small and compact, one of the amine groups is displaced by the anion at 125–180°[12]:

$$H_2B(NR_3)_2^+X^- \longrightarrow H_2XBNR_3 + NR_3 \qquad (4)$$
$$(X = Cl, Br, N_3)$$

In these displacements, it seems probable that amine dissociation is the first step:

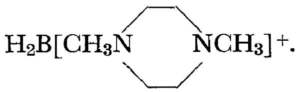
$$H_2B(NR_3)_2^+ \rightleftharpoons H_2BNR_3^+ + NR_3 \qquad (5)$$

In fact, amine exchange can be effected at comparable temperatures, *e.g.*,



$$H_2B(NR_3)_2^+ + R_2NCH_2CH_2NR_2 \rightarrow H_2B(\underset{R}{\overset{R}{N}}CH_2)_2^+ + 2NR_3 \qquad (6)$$

Surely in the amine exchange reaction, a prior dissociation step is necessary because any other reaction course requires sterically improbable intermediates or activated complexes. Relative ease of ligand exchange in the cation classes is sulphide $\gg$ arsine $>$ phosphine $>$ amine $>$ diamine. Sulphide displacements occur rapidly at room temperature, *e.g.*, $H_2B[S(CH_3)_2]_2^+$ and *N*,*N'*-dimethylpiperazine react exothermally to give



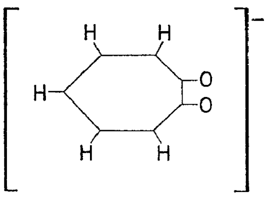
$$H_2B[CH_3N \quad NCH_3]^+.$$

In contrast, amine displacements by diamines require temperatures of at least 150° for reasonable reaction rates.

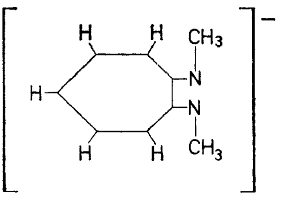
Reactivity does reside in the BH hydrogen atoms of the boronium cations. Abstraction of the hydrogen atoms by certain free radicals follows a well-ordered course to give derivatives of the cation. For example, fluorine reacts with aqueous solutions of $H_2B[N(CH_3)_3]_2^+$ to give $F_2B[N(CH_3)_3]_2^+$. Some peroxides behave in a similar fashion; FSO_2OOSO_2F yields the bis-OSO_2F derivative. Monochlorination and bromination can be effected in aqueous media with the respective halogens; however, the chlorination reaction is quite slow even at 90°. The monochloro derivative can be obtained in excellent conversion with reagents that efficiently supply chlorine radicals, *e.g.*, aqua regia, NCl_3, and SF_5Cl (u.v. irradiation). Iodine monochloride converts the parent cations to the dichloro derivatives, $Cl_2B(NR_3)_2^+$, rather than the iodo derivatives which would be expected in a typical electrophilic ICl reaction. In contrast, the polyhedral borane anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, which are very susceptible to electrophilic attack, yield $B_{10}I_{10}^{2-}$ and $B_{12}I_{12}^{2-}$, respectively, on reaction with ICl[13].

Chelated boronium ions[3, 4]

With the bidentate ligands $\underset{\sim}{T}$ and $\underset{\sim}{A}$ derived from tropolone and *N*,*N'*-dimethylaminotroponeimine, respectively, boron yields the pseudotetrahedral



$\underset{\sim}{T}$



$\underset{\sim}{A}$

(D_{2d}) cations, T_2B^+ and A_2B^+. In dilute aqueous solution, bromide salts of these cations behave as strong 1:1 electrolytes. Both cations are moderately resistant to hydrolysis. For example, T_2B^+ does not undergo significant hydrolysis below 90° and there is no fast ($\sim 10^3$ sec^{-1}) ligand exchange in the presence of tropolone up to 100°. Aqueous base does degrade the bis(tropolono)borane cation and the hydrolysis is reversed on addition of acid. By contrast, the amino cation is unaffected by strong alkali. In fact, $A_2B^+OH^-$ can be prepared by ion exchange methods and it is a strong base. The amino cation is also stable in dilute mineral acid up to 100°. In more concentrated acid, *e.g.* 30 per cent hydrochloric acid, hydrolysis proceeds, although at a very low rate, at 70–100°. Hydrolysis is irreversible. Presumably, in the acid-catalysed hydrolysis of A_2B^+, the initial step comprises attack on a nitrogen atom by a hydronium ion; the rate determining step in the hydrolysis has not been identified.

The hexafluophosphate and chloride salts of the bis(tropolono)borane cation are colourless, the bromide is pale yellow, and the iodide is red-orange. The origin of the colour may be a charge transfer process from anion to chelate cation. Since considerable positive charge is believed (*vide infra*) to be present on the ligands of the cation, ion-pairing in solution should provide sufficient close approach for charge transfer. In aqueous solution, neither T_2B^+ nor A_2B^+ gave polarographic evidence of a facile single electron reduction.

Six-coordinate cations[3,4]

With *N,N′*-dimethylaminotroponeimine, the tetrahalides of silicon, germanium, and tin yield salts of formula $A_3M^+X^-$. These salts are strong electrolytes as evidenced by conductivity studies. The cations resist hydrolysis in neutral or basic media but are subject to acid catalysed hydrolysis. The rate of hydrolysis is high in dilute (1 per cent) mineral acid. Thus, these six-coordinate cations are much more readily decomposed by acid than the four-coordinate A_2B^+ cations. Rates of hydrolysis in 5 per cent hydrochloric acid increase in the series $A_2B^+ \ll A_3Si^+ < A_3Sn^+$. This order may reflect a decreasing steric factor in the rate determining step which may be water insertion. Basicity of the nitrogen atoms also varies significantly among these chelates. The boronium cation, A_2B^+, and hydrogen chloride do not interact over the temperature range of −78 to 30° whereas the pseudo-octahedral cations are all rapidly converted at 25° and below to amine hydrochloride and metal tetrachloride:

$$A_3Si^+Cl^- + 6HCl \longrightarrow 3AH_2{}^+Cl^- + SiCl_4 \tag{7}$$

Silicon tetrachloride reacts with tropolone in aqueous or non-aqueous media to yield $T_3Si^+Cl^-$. Germanium tetrachloride behaves similarly although there is a tendency in non-aqueous media for the reaction to stop with formation of T_2GeCl_2†. Reaction of tin tetrachloride with the sodium salt of tropolone gives T_3SnCl. Unlike the silicon and germanium compositions, T_3SnCl gives no evidence of electrolyte behaviour and is not subject to facile metathetical reactions in which the chlorine atom is replaced. Sublimation of T_3SnCl can be effected at ~300°/0·1 μ. A closely related compound, $T_3SnC_6H_5$, was prepared from phenyltin trichloride and was shown to be monomolecular in dichloromethane solution. Thus, T_3SnCl and $T_3SnC_6H_5$ appear to be seven-coordinate tin structures, at least in the solution and vapour states.

The silicon and germanium cations derived from tropolone are stable in acidic or neutral media; hydrolysis is not significant below 80–100°. Also,

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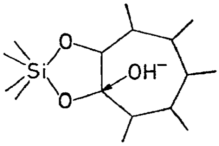
† The sole product from tropolone and tin tetrachloride is T_2SnCl_2 which is isomorphous with T_2GeCl_2. There are eight metal atoms per unit cell in these derivatives; therefore, they cannot be formulated as salts of the type $2T_3M^+MCl_6{}^{2-}$.

there is no rapid ligand exchange in solutions of T_3M^+ and tropolone at 100°. At about 140°, the average lifetime of ligand in the silicon chelate is approximately a millisecond; the lifetime is longer in the germanium chelate. Less stable than these is the phosphorus derivative, T_3P^{2+}, obtained from tropolone and phosphorus pentachloride. This cation begins to hydrolyse in acidic media at temperatures as low as 75°, and the hydrolysis, unlike that for T_3Si^+ and T_3Ge^+, is irreversible. The greater formal charge in T_3P^{2+} which provides a more favourable coulombic attraction for attack of a nucleophile must account for the more facile hydrolysis of this cation. A related chelate cation, $T_2As(OH)_2^+$, is significantly hydrolysed in acidic media at room temperature.

The six-coordinate tropolone cations are rapidly decomposed by hydroxyl ions; this is actually characteristic of all tropolone chelates. An extensive tracer study of chelate hydrolysis in basic solution was made with water enriched in O^{18}. The tropolone produced in the hydrolysis was analysed by mass spectrometry for O^{18} enrichment. Where enrichment occurred, one O^{18} atom was introduced into the tropolone nucleus. In no instance did enrichment occur with a neutral chelate whereas all of the cation complexes yielded enriched tropolone. This unequivocally established hydroxyl ion attack in the cationic chelates on a ligand site, most probably the carbon atom adjacent to the oxygen atom (*Figure 1*):



OH⁻ Attack in T_3Si^+

Figure 1. Probable site for ligand attack by hydroxyl ion in the cationic tropolone chelates

The fraction of ligand enrichment for the various tropolone cations was approximately equal to the charge of the cation divided by the number of ligands per cation.

It would appear from these results that hydroxyl ion attack on the metal tropolonates initiates at the ligand as long as the metal chelate bears a formal positive charge. In this context, the predicted enrichments for the various cations as compared to observed enrichments are:

	Per cent enrichment	
Cation	*Observed*	*Theory*
T_3Si^+	27–28	33
T_3Ge^+	30–33	33
T_2B^+	48	50
T_3P^{2+}	53	67

The data are not sufficiently precise to rule out a minor competing reaction that may be dissociative or involve hydroxyl ion attack on a site such as the central atom. Similar experiments with the silicon tris(dibenzoylmethanide) cation show one-third of the dibenzoylmethane hydrolysate to be enriched. Thus it appears that hydroxyl ion attack in the cationic β-diketone derivatives also starts at the ligand rather than the central atom as originally proposed[14].

All of the T_3M^+ and A_3M^+ cations should have D_3 symmetry and thus have *d* and *l* forms; partial resolution of the closely related cation tris-(acetylacetonato)silicon(IV) has been reported[15]. We are attempting resolution of these cations and hope to study the racemization process in solution and in the solid state.

Eight-coordinate cations[4, 5]

Niobium and tantalum pentachloride react with tropolone in aqueous acid to give the salts $T_4Nb^+Cl^-$ and $T_4Ta^+Cl^-$, respectively, which are strong electrolytes. The niobium chelate decomposes rapidly in water with separation of the seven-coordinate neutral derivative T_3NbO:

$$T_4Nb^+ + OH_2 \longrightarrow T_3NbO + H^+ + TH \tag{8}$$

When this hydrolysis was effected in O^{18} enriched water, the tropolone hydrolysate was not enriched in O^{18}. Hydrolysis of T_4Nb^+ in aqueous base is fast, and all of the tropolone ligands are removed. In the basic hydrolysis with O^{18} tracer, the tropolone is enriched but to an extent three-fifths that expected for initial OH^- attack on the ligand. Apparently reaction (8) is competing with hydroxide ion attack on the ligand in the first step.

The tantalum chelate is far more stable than the niobium derivative. No significant hydrolysis occurs in two weeks at 75° or at 140° in half an hour. Aqueous base rapidly and completely degrades T_4Ta^+. Tracer studies of this basic hydrolysis showed only minor enrichment of the tropolone hydrolysate. This indicates that hydroxyl ion attack on the ligand is a minor reaction course. Since nine-coordinate structures are well established for third row transition metals, the major reaction site in T_4Ta^+ for hydroxyl ion may well be the tantalum atom.

The structures of the T_4Nb^+ and T_4Ta^+ ions have not been established. Hoard and co-workers[16] have shown that in eight-coordinate complexes in which the ligand is a symmetrical bidentate species either one of two structures is generated, the dodecahedral D_{2d} or antiprismatic D_2 model (*Figure 1*). Hoard and Silverton[16] have pointed out that energy differences between the D_{2d} and D_2 models should be small. In fact, although the point group symmetries for the two models are different, relatively minor distortions[16] are required to interconvert these structures (note close similarities in the projections down the related two-fold axes in *Figure 2*). In both models, the four ligands are equivalent. For T_4Ta^+ or T_4Nb^+, none of the five CH hydrogen atoms are equivalent in either the D_{2d} or D_2 model. We suggest that the energy barrier to interconversion of the D_{2d} and D_2 structures is low and that the energy difference between the models is small with respect to packing forces in the solid state. We are exploring the possibility

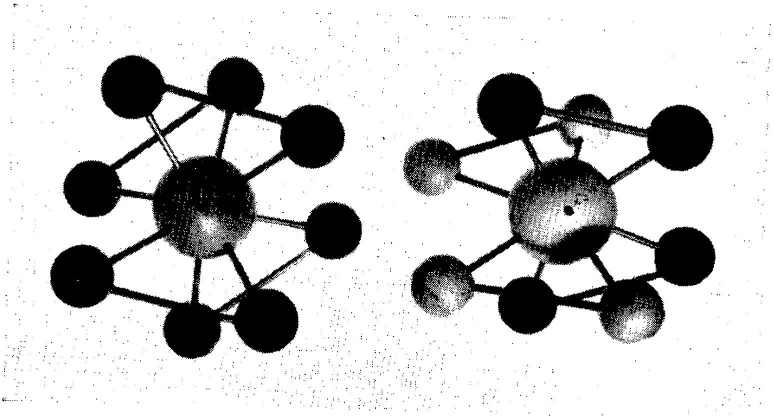


Figure 2. The D_{2d} and D_2 models for T_4Ta^+. The cross-sticks represent the symmetrical bidentate tropolono ligand

that D_{2d} symmetry may prevail in the cation for some $T_4Ta^+X^-$ salts and D_2 symmetry for other salts.

Extensive efforts were made to resolve optical isomers of T_4Ta^+ with optically active anions, but no success was achieved. Optical isomers are possible only in the D_2 model. Unfortunately, the negative experimental results are, strictly speaking, meaningless.

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