solutions in the TFAc melt up to ~1 M; hence, no spectrum for Mn^{2+} is shown in Figure 2.

On the basis of a comparison of the values of the ligand field parameters, the general character of the spectra, and the observed molar absorptivities in Figure 2 and Table I with corresponding data for these same transition metals in aqueous media[3] and in related glassy and molten salts (e.g., nitrates, acetates, sulfates),[4-8] we make the following observations. In appearance, the spectra of the 3d transition metals in the TFAc melt shown in Figure 2 are much like the corresponding spectra of these same transition-metal cations in water where octahedral $M(H_2O)_6^{n+}$ complexes (M^{n+} = transition-metal cation) are known to exist; however, the molar absorptivities in the TFAc melt are roughly twice as high as in aqueous media for V^{3+}, Cr^{3+}, and Fe^{2+} and 4–20 times higher for Co^{2+}, Ni^{2+}, and Cu^{2+}. Also, there is other evidence for oxyanion ligands such as CF_3COO^-, CH_3COO^-, and NO_3^- that complexes of the type MA_4^{n-4} (A = monovalent anion) can exist in both the solid and solution state.[4,9-12] Similar complexes involving the sulfate anion have been reported[5] for Co^{2+} in molten alkali-metal bisulfates, i.e., $Co(O_2SO_2)_4^{6-}$. In these complexes, each oxyanion ligand coordinates to the central metal cation through two of its oxygen atoms, with one of the metal–oxygen (M–O) bonds being shorter than the other. The four oxygen atoms associated with the short M–O bonds and the four associated with the longer M–O bonds form two sets of interpenetrating (somewhat distorted) tetrahedra about the central metal cation. The resulting array of atoms produces an eight-coordinated structure that is approximately dodecahedral.[9-12]

Cotton and Bergman[9] have proposed a principle to account for the quasi-bidentate coordination exhibited by some oxyanions, which is based on the premise that a polyatomic ligand having two or more chemically equivalent coordinating atoms (CECAs) will often tend to interact with the central metal atom through two of the CECAs. Although one of the two "coordinated" oxygen atoms of a given ligand is usually found to lie closer to the central metal cation than the other in the solid state, it is reasonable to suppose that in solution, the two CECAs will, on the average, be equidistant from the central metal cation, leading to a somewhat more symmetrical overall coordination environment than that for the dodecahedral MA_4^{n-4} complexes in the solid state.[9-12]

The implications of the quasi-bidentate MA_4^{n-4} structure with regard to ligand field spectral properties have been reviewed in detail by Johnson and Dickinson.[4] Without repeating their discussion, it is clear that the results in Figure 2 and Table I reflect the same characteristics as those observed for NO_3^- and CH_3COO^- complexes of Co^{2+} and Ni^{2+} under conditions where the MA_4^{n-4} dodecahedral structure was determined to exist. In the case of Co^{2+} in the TFAc melt, we observe the same type spectral behavior by varying temperature (40–120 °C) that was reported by Ingram et al.[6] when alkali acetates were added to Co^{2+} in lead acetate, namely a shift from a pink solution of relatively low molar absorptivity to a blue solution of considerably higher molar absorptivity. Here again, the interpretation was in terms of transformation from a distorted octahedral CoA_6^{4-} complex to the dodecahedral CoA_4^{2-} complex. The existence of the dodecahedral structure in the case of the Co^{2+}–TFAc complex in the TFAc melt is best supported by the X-ray diffraction study of Bergman and Cotton,[10] which showed that the $Co(O_2CCF_3)_4^{2-}$ structure in $[(C_6H_5)_4As]_2[Co(O_2CCF_3)_4]$ is intermediate between tetrahedral and dodecahedral. Johnson and Dickinson[4] observe that the molar absorptivities for Co^{2+} complexes generally decrease as one goes from CoA_4^{2-} (tetrahedral) to CoA_4^{2-} (dodecahedral) to CoA_6^{4-} (octahedral). The peak molar absorptivity for the Co^{2+}–TFAc complex of Figure 2d ($\epsilon \simeq 109$ at 16 800 cm^{-1}) is intermediate between the value reported by Cotton and Bergman[10] for $Co(O_2CCF_3)_2^{2-}$ in acetonitrile ($\epsilon \simeq 200$ at 17 400 cm^{-1}) and the value, e.g., for $Co(H_2O)_6^{2+}$ in aqueous media[3] ($\epsilon \simeq 5$ at 19 600 cm^{-1}) or for Co^{2+} at octahedral sites in $Pb(O_2CCH_3)_2$ glass ($\epsilon \simeq$ 35 at 18 400 cm^{-1}).[6]

The body of information from this study, taken in the context of prior work on related systems,[7] suggests that the V^{3+} and Cr^{3+} cations most probably exist in an octahedral ligand field in the TFAc melt, with some slight distortion causing the twofold increase in molar absorptivity relative to that observed in aqueous media. The absence of any observable features in the spectra of concentrated Mn^{2+} solutions in the TFAc melt shows rather conclusively that Mn^{2+} is in a weak, high-spin ligand field (as expected); nothing more definitive can be said concerning its coordination environment. The Fe^{2+} results in TFAc media are most consistent with octahedral coordination (probably somewhat distorted). Those for Cu^{2+} are interpreted as being due to the MA_4^{n-4} dodecahedral structure based on the relatively high value of the molar absorptivity.

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Registry No. V^{3+}, 22541-77-1; Cr^{3+}, 16065-83-1; Fe^{2+}, 15438-31-0; Co^{2+}, 22541-53-3; Ni^{2+}, 14701-22-5; Cu^{2+}, 15158-11-9; CsTFAc, 21907-50-6; NaTFAc, 2923-18-4; KTFAc, 2923-16-2.

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Formation of a New 1:1 Addition Compound of Borane with Aminoarsine

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Several articles have appeared in the literature describing the synthesis and characterization of the addition compounds formed by the interactions of BX_3 (X = F, Cl, Br, I) and B_2H_6 Lewis acids with phosphines,[1-7] arsines,[2,3,8-11] and stibines.[2,3,9] However,

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Table I. NMR Spectral Data for the 1:1 Addition Compounds I and II[a]

compd	temp, °C	^{11}B NMR, ppm	^{13}C NMR,[b,c] ppm C-1	^{13}C NMR,[b,c] ppm C-2	^{13}C NMR,[b,c] ppm C-3	^1H NMR, ppm H-1	^1H NMR, ppm H-2	^1H NMR, ppm H-3
$\mathrm{Me_2As}\overline{\mathrm{NEt_2{\cdot}B}}\mathrm{H_3}$ (I)	−90	−14.97	50.00 (t of t, 138.8)	13.23 (q, 133.0)	9.88 (q, 126.9)	2.58 (q)	1.04 (t)	1.08 (s)
	−10	−14.97 (q, 97.6)	50.00 (t of t, 138.8)	13.23 (q, 133.0)	9.88 (q, 126.9)	2.58 (q)	1.04 (t)	1.08 (s)
$\mathrm{Me_2}\overline{\mathrm{AsNEt_2{\cdot}B}}\mathrm{H_3}$ (II)	−90	−36.09	40.69 (t, 134.8)	13.92 (q, 125.5)	20.09 (q,[d] 130.9)	2.83 (q)	0.89 (t)	1.05 (s)

[a] $^1J_{X-H}$ coupling constants in Hz are given in parentheses. [b] The ^{13}C chemical shift assignments for I and II [C-1, ($-NC^*H_2CH_3$); C-2, ($-NCH_2C^*H_3$); C-3, [$-As(C^*H_3)_2$]] have been made from the coupled ^{13}C spectra and the chemical shifts of the corresponding parent compound.[c] [c] ^{13}C chemical shift data (ppm) for Me_2AsNEt_2: C-1, 43.91; C-2, 15.00; C-3, 11.93. Significant downfield shifts for C-1 (50.00) in compound I and for C-3 (20.09) in compound II substantiate the assignments. [d] Two methyl resonances observed due to nonequivalence.

Table II. ^{11}B NMR Data on Other Reaction Products[a]

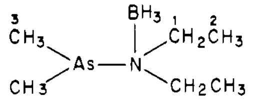
compd	^{11}B NMR, ppm	$^1J_{B-H}$, Hz
$Et_2NH{\cdot}BH_3$[19]	−16.92 (q)	97.6
$Me_2AsH{\cdot}BH_3$[b]	−34.22 (q)	105.4
Me_2AsBH_2[19]	−34.67	
Et_2NBH_2[21]	36.18 (t)	127.7
$(Et_2NBH_2)_2$[21]	1.50 (t)	112.5
μ-$Et_2NB_2H_5$[23]	−19.39 (t of d)	128.5 (BH_2) 34.1 (BH)
$BH_3{\cdot}THF$[19,26]	−1.00 (q)	106.8

[a] Referenced to external $BF_3{\cdot}OEt_2$. [b] The related As–B-bonded compounds $Me_3As{\cdot}BH_3$, $(Me_2As)_2{\cdot}BH_3$, and $Ph_2AsH{\cdot}BH_3$ have similar ^{11}B NMR chemical shifts (−32.2, −33.0, and −29.8 ppm, respectively).[19]

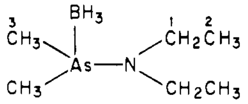
reports describing such interaction with aminoarsines[12] and aminophosphines[13-16] are very limited. In this paper, we report the reaction of $BH_3{\cdot}THF$ with (diethylamino)dimethylarsine, Me_2AsNEt_2. The course of the reaction was followed by temperature-dependent ^{11}B, ^{13}C, and ^1H NMR data. This study indicates the reaction occurs at very low temperatures. Formation of the hitherto unknown 1:1 addition compounds of the aminoarsine with BH_3 is discussed.

Results and Discussion

The reaction between $BH_3{\cdot}THF$-d_8 (formed by reacting B_2H_6 with THF-d_8) and Me_2AsNEt_2 in 1.1:1 molar ratio in THF/toluene solution is essentially complete at −90 °C. Compounds I and II are formed in comparable amounts (Table I). The ^{11}B NMR chemical shift at −14.97 ppm is assigned to I, −2.06 ppm to $BH_3{\cdot}THF$, and −34.63 ppm to II. The ^{13}C NMR chemical shift data for I and II, at −90 °C, are given in Table I. No unreacted aminoarsine was detected. As the reaction solution is allowed to warm gradually, compound II undergoes rearrangement to I and decomposition. The progress of the reaction is monitored by recording the ^{11}B, ^{13}C, and ^1H NMR spectral data from −90 to 25 °C (Tables I and II). The intensity of the −14.97 ppm ^{11}B peak grows with increasing temperature, while the intensity of signals at −2.06 ppm ($BH_3{\cdot}THF$) and −34.63 ppm (II) decrease with increasing temperature. These findings indicate that I is more stable than II or that B–N bond formation is favored over B–As bond formation in the system investigated. This is consistent with the results from previous studies that suggest the following order of adduct stability: $Me_3P{\cdot}BH_3 > Me_3N{\cdot}BH_3 > Me_3As{\cdot}BH_3$.[4,17,18]



I



II

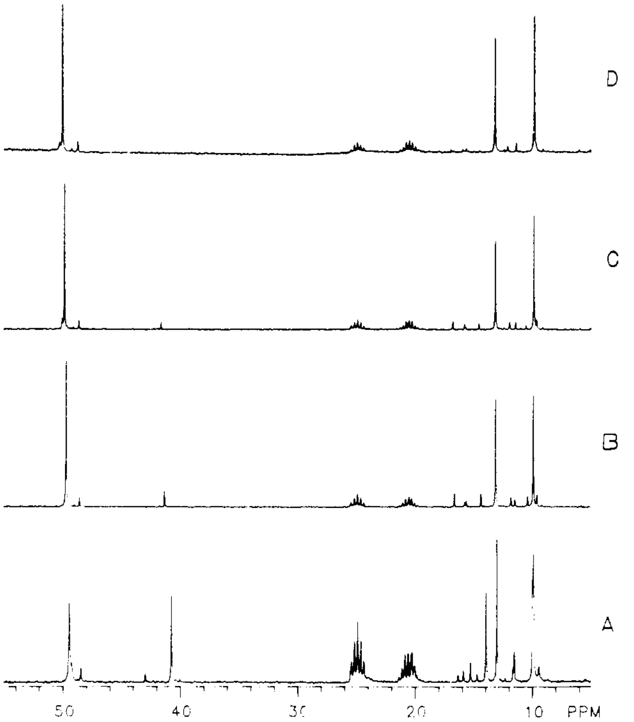


Figure 1. ^{13}C NMR spectra of the reaction mixture at (A) −90 °C, (B) −50 °C, (C) −30 °C, and (D) −10 °C. Chemical shift assignments for I and II are given in Table I.

Also, only P–B bonding occurs in $(Me_2N)_2PF{\cdot}BH_3$[16] and $(Me_2N)_3P{\cdot}BH_3$[6] when both N and P base sites are available. The gradual disappearance of II was followed over the temperature range −70 to −30 °C and was complete at −10 °C (see Figure 1 for ^{13}C NMR spectra). At −10 °C the reaction mixture contained primarily $\mathrm{Me_2As}\overline{\mathrm{NEt_2{\cdot}B}}\mathrm{H_3}$ (I) and only trace amounts of Me_2AsBH_2 and $Et_2NH{\cdot}BH_3$. The latter results from a secondary reaction with excess $BH_3{\cdot}THF$. The species formed as a result of decomposition and rearrangement were identified by ^{11}B NMR data (Table II). The NMR data suggest the reactions (1)–(3) occur.

$$\mathrm{Me_2}\overline{\mathrm{AsNEt_2{\cdot}B}}\mathrm{H_3} \rightarrow \mathrm{Me_2As}\overline{\mathrm{NEt_2{\cdot}B}}\mathrm{H_3} \tag{1}$$

$$\mathrm{Me_2}\overline{\mathrm{AsNEt_2{\cdot}B}}\mathrm{H_3} \rightarrow \mathrm{Me_2AsBH_2} + \mathrm{Et_2NH} \tag{2}$$

$$\mathrm{Et_2NH} + \mathrm{BH_3{\cdot}THF} \rightarrow \mathrm{Et_2NH{\cdot}BH_3} + \mathrm{THF} \tag{3}$$

At 20 °C ^{11}B NMR peaks at 36.18 and −19.39 ppm are noted that indicate the slight decomposition of I, producing $Me_2AsH{\cdot}BH_3$,[19,20] Et_2NBH_2,[19,21] and the μ-hydrido-bridged

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species, μ-$Et_2NB_2H_5$.[19,22–24] The formation of μ-$Et_2NB_2H_5$ occurred slowly at room temperature and continued to take place with time. The formation of these subsequent products can occur via the proposed reaction pathway (4)–(6). Reactions analogous

$$\mathrm{Me_2As\overline{NEt_2{\cdot}B}H_3 \rightarrow Me_2AsH + Et_2NBH_2} \qquad (4)$$

$$\mathrm{Et_2NBH_2 + BH_3{\cdot}THF \rightarrow \mu\text{-}Et_2NB_2H_5 + THF} \qquad (5)$$

$$\mathrm{Me_2AsH + BH_3{\cdot}THF \rightarrow Me_2AsH{\cdot}BH_3 + THF} \qquad (6)$$

to (4) have been observed previously during the decomposition of $F_2AsNMe_2{\cdot}BF_3$[12] and $F_2PNMe_2{\cdot}BF_3$.[16] In solution, compound I decomposed over a period of 3 days to give a product mixture. The ^{11}B NMR spectrum showed the mixture contained approximately 70% μ-$Et_2NB_2H_5$, 25% $Et_2NH{\cdot}BH_3$, a small amount of dimeric $(Et_2NBH_2)_2$,[21,23] and As–B-bonded species such as $Me_2AsH{\cdot}BH_3$ and Me_2AsBH_2[19] (monomeric and/or oligomeric) (Table II). The absence of any $BH_3{\cdot}THF$ and the presence of $(Et_2NBH_2)_2$ in the final product mixture support the formation of μ-$Et_2NB_2H_5$ via eq 5. The substantial yield of $Et_2NH{\cdot}BH_3$, obtained from the initial reaction mixture upon standing, could result from side reactions that involve Et_2NBH_2, Et_2NH, and I. Irreversible decomposition of the addition compounds formed by boranes with molecules having group 15[27] donor atoms are known.[17]

When the reaction was carried out with THF as the solvent, cleavage of the As–N bond and the subsequent rearrangements were facile. These reactions occurred at lower temperatures as compared to those in the previously described reaction. Currently we are investigating the reactions of boron halides, mixed halides, and higher boranes with aminoarsines.

Experimental Section

General Data. Standard high-vacuum line techniques and a Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-493 Dri-Train were used throughout for the handling of all compounds. (Diethylamino)dimethylarsine (bp 80.5 °C (90 mm)) was synthesized by the reaction of Me_2AsCl with excess Et_2NH[25] and was purified prior to use. Diborane(6) was synthesized by the dropwise addition of a diglyme solution of iodine to $NaBH_4$ in diglyme. Trap-to-trap distillation afforded pure diborane(6) in the −126 °C trap. THF-d_8 and toluene-d_8 were purchased from Wilmad Glass Co. and stored over molecular sieves. ^{11}B, ^{13}C, and ^1H NMR spectra were recorded on a Nicolet 300-MHz multinuclear FT NMR spectrometer operating at 96.3, 75.4, and 300.1 MHz, respectively. Chemical shift values for the ^{11}B resonance signals were measured relative to the signal of $BF_3{\cdot}OEt_2$, high-field shifts being taken as negative. The ^1H and ^{13}C NMR chemical shifts were measured with respect to Me_4Si as an internal reference.

Reaction of $BH_3{\cdot}THF$ with Me_2AsNEt_2. A 2.0-mL portion of THF-d_8 and 2.0 mL of toluene-d_8 were placed in the NMR reaction tube (12 mm × 22.5 cm, Pyrex; equipped with a greaseless vacuum stopcock). The tube was evacuated at −196 °C and 2.2 mmol of B_2H_6 condensed into it. The reaction solution was warmed to 20 °C to form $BH_3{\cdot}THF$. The solution was then cooled to −196 °C, and 2 mmol of Me_2AsNEt_2 was condensed onto it. The contents of the tube were shaken gently at −90 °C. The tube was sealed and inserted into the precooled (−90 °C) probe of the NMR spectrometer. The NMR spectra of the reaction solution were recorded from −90 to +25 °C). The NMR spectral assignments are tabulated in Tables I and II.

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(27) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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Direct Synthesis of Potassium Tris(oxalato)manganate(III) and First Synthesis of Alkali-Metal and Ammonium Trifluoro(oxalato)manganates(III)

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The compound $K_3[Mn(C_2O_4)_3]{\cdot}3H_2O$, known for quite some time,[1] has served as a very oft-quoted example whenever the subject of inorganic photochemistry is discussed.[2] The method involving the reaction of $KMnO_4$ with oxalic acid and $K_2C_2O_4$ in the presence of an excess of K_2CO_3 is universally accepted for the synthesis of $K_3[Mn(C_2O_4)_3]{\cdot}3H_2O$. This method requires very careful manipulation and uses an excess of K_2CO_3 in order to control the pH. The chances of contamination of the end product, owing to the use of K_2CO_3 in such quantities, cannot be ruled out. It is possible to synthesize $K_3[Mn(C_2O_4)_3]{\cdot}3H_2O$ in a more nearly quantitative way directly from MnO(OH) without making use of any buffer. It will also be shown that $[Mn(C_2O_4)_3]^{3-}$ can exist in solutions in the presence of countercations like Na^+, Rb^+, Cs^+ or NH_4^+. Attempts to stabilize manganese(III)–oxalate systems have now led to the first synthesis of alkali-metal and ammonium trifluoro(oxalato)manganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K or NH_4), providing a very good opportunity to demonstrate the enhanced stability of (oxalato)manganates(III) and to obtain a set of internally consistent data concerning the effect on the magnetic properties of trivalent manganese on going from $K_3[Mn(C_2O_4)_3]$ to $A_2[MnF_5]$ via $A_2[MnF_3(C_2O_4)]$.

Experimental Section

The chemicals used were all reagent grade products. The compound MnO(OH) was prepared by the oxidation of $Mn(OH)_2$ with hydrogen peroxide.[3]

Infrared spectra were recorded on a Perkin-Elmer Model 683 spectrophotometer. Electronic spectra were recorded on a Beckman Model UV-26 spectrophotometer. The Gouy method was used to measure the magnetic susceptibility of the complexes using $Hg[Co(NCS)_4]$ as the standard.

Syntheses. Potassium Tris(oxalato)manganate(III) Trihydrate, $K_3[Mn(C_2O_4)_3]{\cdot}3H_2O$. To a water suspension (20 cm^3) of 0.89 g (10.1 mmol) of MnO(OH) was added a concentrated solution of 2.82 g (15.3 mmol) of $K_2C_2O_4$. The mixture was cooled in an ice bath for ca. 15 min, followed by addition of a concentrated solution of 1.93 g (15.3 mmol) of oxalic acid. The solution was stirred for ca. 50 min in an ice bath. The solution, which became cherry red, was filtered quickly, and an excess of precooled (~0 °C) ethanol (about 1/1 v/v) was added with stirring to obtain the cherry red $K_3[Mn(C_2O_4)_3]{\cdot}3H_2O$. The microcrystalline compound was isolated by quick filtration, washed twice with precooled ethanol, and finally dried in vacuo in the absence of light. The yield of $K_3[Mn(C_2O_4)_3]{\cdot}3H_2O$ was 3.1 g (62.5%).

Alkali-Metal and Ammonium Trifluoro(oxalato)manganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K, NH_4). Representative Procedure. Freshly prepared MnO(OH) was dissolved in 40% HF with maintenance of the molar ratio of MnO(OH) to HF at 1/4–5 (2.5 cm^3, 40% HF/1 g of MnOOH), and the solution was warmed at ca. 100 °C for ca. 5 min, followed by filtration. The filtrate was cooled to room temperature, and a concentrated solution of $A_2C_2O_4$ (A = Na, K, NH_4) was slowly added with stirring, with the molar ratio of MnO(OH) to $A_2C_2O_4$ being maintained at 1/1. The solution was stirred for a further period of ca. 10 min at room temperature (ca. 20 °C). Addition of an excess of ethanol, in an amount not exceeding half of the original volume of the solution, precipitated pink alkali-metal or ammonium trifluoro(oxalato)manganage(III), $A_2[MnF_3(C_2O_4)]$. The compound was separated by filtration, washed thrice with ethanol, and finally dried in vacuo. Starting from 1.0 g of MnO(OH) in each case, the yields of $Na_2[MnF_3(C_2O_4)]{\cdot}5H_2O$, $K_2[MnF_3(C_2O_4)]{\cdot}H_2O$, and $(NH_4)_2[MnF_3(C_2O_4)]$ were 3.4 g (89%), 3.2 g (94%), and 2.4 g (90%), respectively. Anal. Calcd for

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