destruction of the –V–O–V– bridging system and the formation of monomers.

In view of the apparent structure of the compounds reported here, it was of interest to determine their molecular weights. This work was frustrated by the low solubility of the compounds in suitable solvents. Livingstone and coworkers[2] formulated VO(ttmbs)$_2$ as a dimer, based on a cryosopically determined molecular weight of 910 (calculated for dimer 1082) in nitrobenzene; however, the low solubility of VO(ttmbs)$_2$ in nitrobenzene suggests that this figure may be subject to considerable error. By using a vapor pressure osmometer we have obtained values ranging from 720 to 810 in methylene chloride as the solvent. Again the solubility is such that the results are of questionable accuracy. For VO(nebas)$_2$ we have obtained values that are close to that calculated for the monomer. This suggests that even in noncoordinating solvents the –V–O–V– bridging is disrupted upon dissolution with the formation of either monomers or an equilibrium mixture of monomers and more highly bridged species. This same type of phenomenon was also observed in the case of VO(sal)$_2$(+)tnCH$_3$, where the V=O stretching frequency was observed at 991 cm^{-1} in chloroform solutions.[9]

The magnetic moments of the subject complexes at room temperature compare with the spin-only value and the solution esr parameters are similar to those that we have reported previously for VO(mtdk)$_2$ complexes. Optical spectra of VO(ttmbs)$_2$ are shown in Figure 2. Similar spectra were exhibited by VO(nebas)$_2$, as indicated in Table I. The diffuse reflectance spectra differ considerably from those observed for the previously reported square-pyramidal compounds, again emphasizing the structural differences in the solid state. Solutions of both VO(ttmbs)$_2$ and VO(nebas)$_2$ in pyridine exhibit electronic spectral properties which are essentially identical with those previously reported for the square-pyramidal VO(mtdk)$_2$ complexes dissolved in pyridine. Again this observation is consistent with the notion that the solid-state bridged structure is broken down by strong donor solvents with the concomitant formation of monomeric pyridine adducts.

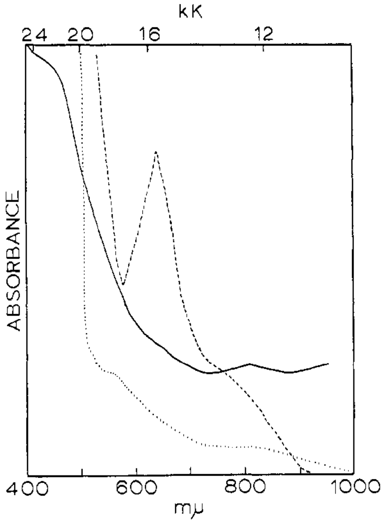

Figure 2.—Optical spectra of VO(ttmbs)$_2$: ——, diffuse reflectance; – – –, pyridine; · · · ·, methylene chloride.

The most obvious difference between the ligands that form monomeric complexes and those that give rise to extended structures is that the latter ligands have electron-withdrawing groups present. In VO(ttmbs)$_2$ and VO(nebas)$_2$ the electron density on the vanadium atoms may be reduced by the electron-withdrawing groups to such an extent that the increased Lewis acidity of the vanadium atoms makes –V–O–V– bridging possible.

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Complexes of Maleonitriledithiolate with Metals of Group III

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Complexes of transition metals with ligands containing the *cis*-1,2-enedithiol structural unit[1] have been the subject of numerous studies in the past 10 years. The field has been reviewed several times.[2]

A few reports of complexes of dithiolene ligands with posttransition metals have appeared.[3] Tuck and coworkers[3c,4] have described salts of the anions In(mnt)$_2^-$ and In(mnt)$_3^{3-}$, where mnt^{2-} is the ligand maleonitriledithiolate, *cis*-1,2-S$_2$C$_2$(CN)$_2^{2-}$. They also have reported briefly the results of a crystal structure study of the six-coordinate tris complex.[3c] We wish now to present results which supplement and extend those of Tuck and coworkers.

Reaction of the sodium salt of the ligand with thallium(III) chloride in a ratio of 3:1 or greater gave salts of the six-coordinate tris complex ion Tl(mnt)$_3^{3-}$. Similarly, reaction of Na$_2$mnt with indium(III) chloride in a 3:1 ratio led to salts of the previously reported[3c,4] complex ion In(mnt)$_3^{3-}$. It was found that salts of Tl(mnt)$_3^{3-}$ also could be prepared more conveniently by reaction of thallium(I) bromide or acetate with an excess of Na$_2$mnt in the presence of atmospheric oxygen.

When the ratio of reactants was 2:1, reaction of mnt^{2-} with tetrabromothallate yielded products having the composition Q$_2$Tl(mnt)$_2$Br, where Q is a quaternary ammonium cation. From the analogous reaction

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[1] The name dithiolene has been suggested for this class of ligand by McCleverty.[2b]

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TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES FOR GROUP IIIb MALEONITRILEDITHIOLATE COMPLEXES

	Mp, °C	% C		% H		% N		% S		% halogen		Equiv conductance[a]
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$[(C_2H_5)_4N]Ga(mnt)_2$	135.0–135.2	40.04	40.13	4.19	4.35	14.58	14.48	26.70	26.47			129[b]
$[(CH_3)_4N]_2In(mnt)_2Cl$	225.0–226.0	33.19	33.23	4.17	4.27	14.52	14.47	22.15	22.43	6.12	6.35	149
$[(C_2H_5)_4N]_2In(mnt)_2Cl$	148.0–148.3	41.69	41.76	5.83	5.88	12.16	11.90	18.56	18.87	5.13	4.97	154
$[(C_2H_5)_4N]_3In(mnt)_3$	166.5–167.0	46.70	46.87	6.53	6.45	13.61	13.58	20.74	20.92			121
$[(n\text{-}C_4H_9)_4N]Tl(mnt)_2$	160.0–161.0	39.65	39.50	4.79	5.11	9.63	9.65	17.60	17.68			110
$[(n\text{-}C_4H_9)_4N]_2Tl(mnt)_2Br$[c]	103.0–104.0	45.95	45.77	6.96	6.92	7.94	8.01	11.99	12.22	7.80	7.61	149
$[(n\text{-}C_4H_9)_4N]_3Tl(mnt)_3$	143.0–143.5	53.30	53.31	8.05	8.15	9.32	9.10	14.20	14.32			95
$[(C_2H_5)_4N]_3Tl(mnt)_3$	193.0–194.0	42.58	42.39	5.95	6.16	12.31	12.61	18.91	19.25			120
$[(CH_3)_4N]_3Tl(mnt)_3$	231.0–232.0	34.01	34.58	4.28	4.56	14.87	15.06	22.70	22.31			126

[a] 0.001–0.002 M in acetonitrile; cm²/mol ohm. [b] 0.0039 M in acetonitrile. [c] Tl: calcd, 19.47%; found, 19.49%.

of indium(III) chloride we isolated products having the formula $Q_2In(mnt)_2Cl$.

We were unable in any case to isolate bis complexes $QM(mnt)_2$ ($M = In, Tl$) from solutions containing halide ions; $Q_2M(mnt)_2X$ or $Q_3M(mnt)_3$ always was obtained. However, $QTl(mnt)_2$ was obtained by reaction of Na_2mnt with thallium(III) acetate in a 2:1 ratio, in the presence of a quaternary ammonium nitrate. If the complexes $Q_2M(mnt)_2X$ contain five-coordinate metal, both acetate and nitrate must coordinate less strongly than halide in these systems.

It has been reported that $In(mnt)_2^-$ forms adducts with bidentate nitrogen and phosphorus donor ligands.[3c,4] With the exception of an unstable adduct of dimethylacetamide, no adducts with unidentate ligands were observed.[3c,4] Dithiolene complexes in which halogen remains coordinated to any metal are rare.[5]

Very recently Tuck and Yang[4] have reported the details of their preparation of $[(C_2H_5)_4N]In(mnt)_2$. Their procedure is nearly identical with ours for preparing $[(C_2H_5)_4N]_2In(mnt)_2Cl$. Analytical data for both compounds are good and indicate that both are correctly formulated.

The only significant difference in procedure seems to be that Tuck and Yang[4] used solvents containing considerable amounts of water, both for preparation and for recrystallization, while our solvents for both processes are anhydrous. In the light of our conductivity data (*vide infra*), which suggest that in polar solvents the halide is not coordinated, the difference in results is not unreasonable.

Reaction of Na_2mnt in any ratio with a pyridine solution of anhydrous gallium(III) chloride gave $QGa(mnt)_2$ as the only isolable product.

Equivalent conductances of the mnt complexes in acetonitrile solution have been determined (Table I). It is not possible to decide conclusively from conductance measurements at a single concentration whether or not the halogen of $Q_2M(mnt)_2X$ is coordinated to the metal in solution.[6] However, it is known that equivalent conductance is generally higher for salts of small anions such as halide than for large, bulky complex anions.[7] The fact that equivalent conductance values are generally similar for $QM(mnt)_2$ and $Q_3M(mnt)_3$ but substantially higher for $Q_2M(mnt)_2X$ suggests that the halide does not remain coordinated in acetonitrile solution. Analytical data for the complexes prepared in this work are set out in Table I.

Experimental Section

Disodium maleonitriledithiolate was prepared by the method of Bähr and Schleitzer[8] as modified by Davison and Holm.[9] Quaternary ammonium halides and nitrates were Eastman reagent. The compounds $GaCl_3$, $InCl_3$, TlCl, TlBr, TlOAc, and $Tl(OAc)_3$ were from Alfa Inorganics, Inc. Microanalyses for carbon, hydrogen, nitrogen, sulfur, and halogen were by Galbraith Laboratories, Inc.

$[(C_2H_5)_4N]_2In(mnt)_2Cl$.—Disodium maleonitriledithiolate (1.90 g, 0.0102 mol) was dissolved in 30 ml of methanol. To this solution was added 1.13 g (0.0050 mol) of indium(III) chloride dissolved in 30 ml of methanol. The mixture was filtered into a flask containing 1.60 g (0.010 mol) of tetraethylammonium chloride in methanol. The solution was filtered, and the precipitated product was recrystallized from ethanol. The tetramethylammonium salt was prepared similarly and was recrystallized from ethanol.

$[(C_2H_5)_4N]_3In(mnt)_3$.—The procedure was essentially the same as for the chlorine-containing product, except that the mole ratio $InCl_3{:}Na_2mnt{:}(C_2H_5)_4NCl$ was 1:3:3. The product was recrystallized from methanol.

$[(C_2H_5)_4N]_3Tl(mnt)_3$.—Thallium(III) chloride was prepared by chlorinating thallium(I) chloride in acetonitrile.[10] Reaction of $TlCl_3$ or $Tl(OAc)_3$ with Na_2mnt and $(C_2H_5)_4NCl$ in the mole ratio 1:3:3 was carried out as for the indium analog. The product was recrystallized from methanol. The tetramethylammonium salt was prepared similarly and was recrystallized from methanol. The tetra-*n*-butylammonium salt was prepared analogously from thallium(III) acetate, tetra-*n*-butylammonium bromide, and Na_2mnt.

$[(n\text{-}C_4H_9)_4N]_3Tl(mnt)_3$ from TlBr.—A solution of 3.72 g (0.020 mol) of disodium maleonitriledithiolate in methanol was added to a suspension of 2.84 g (0.010 mol) of thallium(I) bromide in methanol. The mixture was filtered, and a methanol solution of 5.30 g (0.017 mol) of tetra-*n*-butylammonium bromide was added. The solution was concentrated by means of a rotary evaporator, and the red crystalline product was filtered and recrystallized three times from methanol.

$[(n\text{-}C_4H_9)_4N]_2Tl(mnt)_2Br$.—A solution of 7.25 g (0.034 mol) of disodium maleonitriledithiolate and 25.25 g (0.078 mol) of tetra-*n*-butylammonium bromide in 40 ml of methanol was stirred under nitrogen for 1 hr and then filtered. A solution of 10.0 g (0.013 mol) of tetra-*n*-butyltetrabromothallate[10] in 30 ml of a 1:1 tetrahydrofuran–methanol mixture was added to the filtrate dropwise with stirring. The red solution was concentrated under vacuum and filtered. The orange-red product was recrystallized from 1:1 tetrahydrofuran–methanol.

A sample of the complex was decomposed by heating with a concentrated nitric–sulfuric acid mixture to destroy the organic constituents and was analyzed for thallium.[11] *Anal.* Calcd for $C_{40}H_{72}N_6S_4BrTl$: Tl, 19.47. Found: Tl, 19.49.

$[(n\text{-}C_4H_9)_4N]Tl(mnt)_2$.—In a glove box filled with dry nitrogen 1.90 g (0.0050 mol) of thallium(III) acetate was dissolved in dry, cold methanol and combined with a solution of 1.86 g (0.010 mol)

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of disodium maleonitriledithiolate. To this solution was added a methanol solution of 1.52 g (0.0050 mol) of tetra-*n*-butylammonium nitrate. The precipitated product was filtered and recrystallized from ethanol.

$[(C_2H_5)_4N]Ga(mnt)_2$.—Anhydrous gallium trichloride (3.74 g, 0.020 mol) was sublimed into 50 ml of dry pyridine. To the resulting solution was added 7.82 g (0.040 mol) of disodium maleonitriledithiolate and 3.48 g (0.020 mol) of tetraethylammonium chloride dissolved in methanol. The mixture was allowed to stand in the refrigerator for 2 days. The precipitated product was filtered and recrystallized from isopropyl alcohol.

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Perhaloalkyl Hypochlorites. V. Perfluoroalkyl Borate Esters from Reactions with Boron Trichloride[1]

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Fluoroalkyl borate esters have been prepared from reactions of fluorinated alcohols and boron trichloride[2-4] and from the reactions of sodium borohydride with hexafluoroacetone[5]

$$3CF_3CH_2OH + BCl_3 \longrightarrow (CF_3CH_2O)_3B + 3HCl \qquad (1)$$

$$3(CF_3)_2CO \xrightarrow[2.\ H^-]{1.\ BH_4^-} [(CF_3)_2CHO]_3B \qquad (2)$$

Perhaloalkyl borate esters result when boron halides other than boron fluorides are added to hexafluoroacetone[6] or hexafluorocyclobutanone[7]

$$3(CF_3)_2CO + BCl_3 \longrightarrow [(CF_3)_2CClO]_3B \qquad (3)$$

$$3(CF_2)_3CO + BCl_3 \longrightarrow [(CF_2)_3CClO]_3B \qquad (4)$$

Several investigators have observed that the haloalkyl borate esters have greater Lewis acidities than their alkyl counterparts,[2,4,6] a consequence attributed to inductive effects which decrease interaction of the electron pairs on oxygen with the empty p_z orbital on boron.

There have been no reports of *per*fluoroalkyl borate esters (these should be the most acidic alkyl borates according to inductive arguments), and the usual methods of synthesis are not available; *i.e.*, primary and secondary perfluoro alcohols are generally inaccessible, and boron–fluorine bonds do not add across the carbon–oxygen double bond of perfluorinated carbonyl compounds.[6,7]

In our studies of perhaloalkyl hypochlorites, we have discovered a novel reaction with boron trichloride in which chlorine is oxidatively displaced from boron yielding the first perfluoroalkyl borate esters.

Experimental Section

Standard vacuum line procedures with a Monel–Kel-F or glass vacuum system were used throughout. The reaction vessels were Type 304SS cylinders of either 30- or 225-cm^3 capacity.

Reagents.—Carbonyl fluoride was prepared by the reaction of phosgene and NaF at 150° in a 500-cm^3 stainless steel cylinder and was purified by vacuum-line fractionation. Hexafluoroacetone was obtained from Allied Chemical Corp. (Specialty Chemical Division), and nonafluoro-*tert*-butyl alcohol was prepared by antimony pentafluoride fluorination of $CCl_3C(CF_3)_2OH$.[8,9] Chlorine monofluoride was obtained from the Ozark-Mahoning Co., and BCl_3, $(CH_3)_3N$, and NH_3 were obtained from the Matheson Co. and carefully purified before use. Trifluoromethyl, heptafluoroisopropyl, and nonafluoro-*tert*-butyl hypochlorites were prepared by chlorofluorination of F_2CO, $(CF_3)_2CO$, and *tert*-C_4F_9OH, respectively, by previously described methods.[10,11]

Nonafluoro-*tert*-butyl Borate.—The reaction cylinder was charged with $(CF_3)_3COCl$ (10.8 mmol) and BCl_3 (3.4 mmol) at −196°. The materials were allowed to warm to room temperature and shaken for 20 hr. The product mixture was then fractionated through −23, −80, and −196° traps. The −196° fraction contained 9.8 mmol of essentially pure Cl_2. The −80° fraction contained a small amount of $(CF_3)_3COH$ (impurity in starting hypochlorite), and the −23° fraction contained transparent, soft crystals of $(tert\text{-}C_4H_9O)_3B$. The solid melts at 35° and has a vapor pressure of about 1 mm at 25°. The gas-phase infrared spectrum of the solid was obtained in a heated cell (60°) and is tabulated below. The fluorine-19 nmr spectrum was a singlet at +68.1 ppm with respect to CCl_3F while the boron-11 nmr spectrum consisted of a singlet at −13.4 ppm with respect to $BF_3O(C_2H_5)_2$. Although the molecular ion was not observed in the mass spectrum at *m/e* 716 or 715, $(tert\text{-}C_4F_9O)_2(tert\text{-}C_4F_8O)^{11}B^-$ and $(tert\text{-}C_4F_9O)_2(tert\text{-}C_4F_8O)^{10}B^+$ at *m/e* 697 and 696 and other expected ions at *m/e* 628–627 ($^{11}BC_{11}F_{23}O_3^+$, $^{10}BC_{11}F_{23}O_3^+$), 609–608 ($^{11}BC_{11}F_{22}O_3^+$, $^{10}BC_{11}F_{22}O_3^+$), and 481–480 ($^{11}BC_8F_{18}O_2^+$, $^{10}BC_8F_{18}O_2^+$) were present in the 4:1 intensity required of ions containing one boron atom. Ir spectrum (cm^{-1}): 1422 (mw), 1396 (s), 1288 (vs), 1202 (w), 1150 (m), 1124 (m), 988 (s), 952 (mw), 730 (m), 534 (w).

Heptafluoroisopropyl Borate.—The reaction cylinder was charged with $i\text{-}C_3F_7OCl$ (16.0 mmol) and BCl_3 (4.9 mmol) at −196°. The materials were allowed to warm to −20° and stand for 40 hr. Fractionation through traps held at −45 and −196° effected separation of reaction products. The −196° fraction contained 16.7 mmol of Cl_2 contaminated with traces of $(CF_3)_2CO$, BF_3, $CF_3C(O)F$, and CF_3Cl (the latter two materials are known decomposition products of $i\text{-}C_3F_7OCl$). The −45° fraction contained clear, colorless, liquid $(i\text{-}C_3F_7O)_3B$ which had a vapor pressure of about 10 mm at 25°. The infrared spectrum, obtained in the gas phase, showed no $(CF_3)_2CO$ or BF_3; the spectrum is tabulated below. The fluorine-19 nmr spectrum consisted of a doublet at +82.3 ppm (J_{FF} = 2.8 Hz) and a complex signal at +137.4 ppm relative to CCl_3F. Integration of the signals gave a ratio of 6:1 as expected for $i\text{-}C_3F_7O\text{–}$. The product composition was further verified in several experiments by allowing samples to decompose at 25° over a period of several hours or at −20° over a period of several weeks to the expected amounts of $(CF_3)_2CO$ and BF_3 in a 3:1 ratio according to the equation

$$(i\text{-}C_3F_7O)_3B \longrightarrow BF_3 + 3(CF_3)_2CO \qquad (5)$$

Ir spectrum (cm^{-1}): 1439 (ms), 1408 (s), 1315 (vs), 1255 (vs), 1198 (m), 1177 (s), 1122 (s), 1002 (vs), 788 (w), 736 (ms), 720 (m).

Trifluoromethyl Borate.—A reaction cylinder was charged

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