iodide spectra are found in the second (≈13,000 cm^{-1}) and fourth bands (≈20,000 cm^{-1}). Previous studies[8] have shown that these two bands are the most sensitive to the strength and symmetry of the field produced by the ligands.

It is therefore proposed that the complexes [Co(tren)I]I and [Co(tren)(NCS)]SCN are five-coordinated, with tren acting as a tetradentate ligand.

Infrared spectra give additional support to this formulation for the thiocyanate compound. This complex exhibits two bands at 2085 and 808 cm^{-1}, which are attributed to the CN and CS stretching frequencies of the N-bonded NCS ion.[9] Another band found at 2060 cm^{-1} is assigned to the CN stretching frequency of the free SCN$^-$ ion.[9] The CS frequency of the free SCN$^-$ ion usually occurs at about 745 cm^{-1} but is presumably masked by the absorption bands of the ligand in this region.[10] The frequencies exhibited in the [Co(tren)(NCS)]SCN infrared spectrum are almost the same as those found for [Cu(tren)(NCS)]SCN, whose structure has recently been found to be five-coordinated by X-ray crystal structure studies.[11] The copper complex exhibits bands at 2095, 2060, and 818 cm^{-1}.[12]

In conclusion, the tren complexes of cobalt(II), copper(II),[4,11] and probably zinc(II)[3] can exhibit the unusual coordination number five. In contrast, X-ray studies[13] and spectral evidence[14] indicate that all of the nickel–tren complexes which have been studied are octahedral. The structural studies of manganese(II) and iron(II) complexes with tren are sparse but, at least in aqueous solution, seem to indicate octahedral structures.[3] This is in accord with the results of a calorimetric study[15] of the relative stability of five- and six-coordination of bivalent metals from manganese to zinc. The results show that five-coordination is favored in the order (Co, Cu, Zn) > (Fe, Ni) > Mn. The stereochemical requirements of tren thus allow five-coordination for the three elements forming the most stable five-coordinated complexes. By increasing the bulkiness of the ligand through N-methylation, five-coordinated complexes for all of the transition metal ions from manganese(II) to zinc(II) are obtained.

Experimental Section

The complexes [Co(tren)X]X, where X = I or NCS, were prepared by the procedure of Barclay and Barnard[1] and analyzed satisfactorily for nitrogen. The absorption spectra were recorded with a Beckman DK2 spectrophotometer and 5-cm silica cells. The solutions of the complexes in nitroethane were about 10^{-3} *M*. The diffuse-reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference. The infrared spectra were recorded on Nujol mulls using a Perkin-Elmer 337 spectrophotometer. The conductivity values were measured on a WTW Model LBR/B conductivity bridge. All operations on the solutions were performed in an atmosphere of pure nitrogen.

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Bis(tetrahydrofuran)–Haloalanes

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Mono- and diamine adducts of alane, AlH$_3$, and haloalanes are known and have been investigated;[1–4] however, little is known about their ether adducts. Alane does not form well-defined diethyl etherates[5] and the bis(tetrahydrofuran) adduct[6] is reported to be stable only below −5°. The present study concerns the preparation and characterization of some new, crystalline bis- and tris(tetrahydrofuran)–haloalanes.

Experimental Section

Reactants and products were handled in a dry nitrogen atmosphere. All solvents were distilled over lithium tetrahydroalanate, LiAlH$_4$, or sodium metal. The aluminum halides were purified by high-vacuum sublimation. The diethyl ether solvated hydride was prepared according to Schlesinger[5] by using a 3:1 stoichiometric ratio of LiAlH$_4$ and aluminum chloride, AlCl$_3$.

Elemental analyses were performed in our laboratories. Hydrolyses yielded active hydrogen and deuterium which were measured using a vacuum rack equipped with a Toepler pump and a calibrated system. Mass spectrometry confirmed the identity of the evolved gas. The nuclear magnetic resonance spectra were obtained from solutions on a Varian A-60 HR spectrometer. Infrared spectra were obtained on a Beckman IR 9 and IR 11. Fluorolube mulls were used for the 3800–1330-cm^{-1} region; Nujol mulls were used below 1330 cm^{-1}. X-Ray powder diffraction patterns were obtained using Cu Kα radiation with a Debye–Scherrer camera having a 7.16-cm radius. The cryoscopic molecular weights in benzene were obtained using a modified standard apparatus[7] containing a magnetic stirrer and loaded in a drybox. The freezing points were measured using a thermocouple and were reproducible to ±0.01°. Ebulliometric molecular weights were obtained using a differential ebulliometer with thermopiles reproducible to ±0.005°.

(1) **Preparation of AlHX$_2$·2(THF) and AlH$_2$X·2(THF) (X = Cl, Br, I). Method A.**—The preparation of AlHX$_2$·2(THF) and AlH$_2$X·2(THF) requires the reaction of AlX$_3$ and AlH$_3$ in mole ratios of 2:1 and 1:2, respectively. For a typical example, AlHX$_2$·2(THF) was prepared by adding 0.10 mole of solid alumi-

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num halide to 0.05 mole of solid etherated AlH_3. After cooling the mixture to Dry Ice temperature, 250 ml of diethyl ether was slowly added with stirring. The resulting mixture was allowed slowly to warm with stirring until the aluminum halide dissolved, and then 100 ml of tetrahydrofuran (THF) was added. When the solution cleared, the solvent was removed under reduced pressure and dried under high vacuum for 1 hr. Quantitative yields were obtained.

(2) **Preparation of $AlHCl_2 \cdot 2(THF)$, $AlH_2Cl \cdot 2(THF)$, $AlDCl_2 \cdot 2(THF)$, and $AlD_2Cl \cdot 2(THF)$. Method B.**—The preparation of these compounds requires the reaction of $LiAlH_4$ or $LiAlD_4$ with $AlCl_3$ in a ratio of 1:3 for the dichloride and 1:1 for the monochloride. For a typical example, $AlHCl_2 \cdot 2(THF)$ was prepared by dissolving 16.45 g (0.123 mole) of $AlCl_3$ in 125 ml of diethyl ether and adding 1.56 g (0.041 mole) of $LiAlH_4$ in 100 ml of diethyl ether. The solution was filtered to remove the LiCl and 100 ml of THF was slowly added. During the initial THF addition an exotherm occurred which caused the solution to boil. After 20 min, the crystallization was complete and a yield of 12 g (60%) was obtained.

(3) **Preparation of $AlHCl_2 \cdot 2(THF)$ and $AlH_2Cl \cdot 2(THF)$ by the Reaction of $LiAlH_4$ or $NaAlH_4$ with HCl. Method C.**—The preparation of these compounds requires the reaction of $LiAlH_4$ or $NaAlH_4$, sodium tetrahydroalanate, with HCl in a ratio of 1:2 for the dichloride and 1:3 for the monochloride. For a typical example, $AlHCl_2 \cdot 2(THF)$ was prepared by allowing 0.05 mole of $LiAlH_4$ in 600 ml of diethyl ether to react with 0.15 mole of HCl. The LiCl was filtered off and 25 ml of THF was added. After removing the solvent under vacuum, a quantitative yield of $AlHCl_2 \cdot 2(THF)$ was obtained.

(4) **Preparation of $AlH_2I \cdot 2(THF)$ and $AlD_2I \cdot 3(THF)$. Method D.**—The preparations of these compounds require the reaction of AlH_3 or AlD_3 with I_2 in a 2:1 mole ratio. In a typical reaction, 0.03 mole of AlH_3 in 100 ml of THF was added to 3.80 g of I_2 (0.015 mole) in 100 ml of THF. After 1 hr, a crystalline material was isolated and then dried under high vacuum for 3 hr. The yield was 6.8 g (69%).

(5) **Preparation of $AlHClBr \cdot 2(THF)$ and $AlHClI \cdot 2(THF)$.**—These compounds were prepared using a procedure similar to method A except a 1:1:1 mole ratio of AlH_3, $AlCl_3$, and $AlBr_3$ or AlH_3, $AlCl_3$, and AlI_3 was used.

TABLE I

PROPERTIES AND ANALYSES OF HALOALANE ADDUCTS

	Anal, %														
	Calcd						Found						Active H, %		Mp,
Compound	C	H	Al	Cl	Br	I	C	H	Al	Cl	Br	I	Calcd	Found	°C
$AlHCl_2 \cdot 2(THF)$	39.52	7.05	11.10	29.16			38.89	6.93	11.26	29.80			0.76	0.75	90–95
$AlDCl_2 \cdot 2(THF)$	39.37	7.43[a]	11.05	29.05			38.39	7.15	11.45	29.34			0.82	0.78[c]	86–89
$AlH_2Cl \cdot 2(THF)$[b]	44.99	8.53	13.65	17.94			44.67	8.46	13.66	18.00			0.96	0.95	91–93
$AlD_2Cl \cdot 2(THF)$	45.62	9.56[a]	12.81	16.83			44.32	9.47	13.00	18.45			1.91	1.92[c]	93–95
$AlHBr_2 \cdot 2(THF)$	28.94	5.16	8.13		48.13		28.42	5.02	8.20		48.95		0.30	0.26	64–67
$AlH_2Br \cdot 2(THF)$	37.95	7.16	10.66		31.59		37.80	7.25	10.85		31.65		0.79	0.79	83–85
$AlHI_2 \cdot 2(THF)$	22.75	4.02	6.33			59.58	22.50	4.01	6.29			59.80			133–134
$AlH_2I \cdot 2(THF)$	32.02	6.04	8.99			42.29	32.05	6.12	8.84			41.35			165–166
$AlHClBr \cdot 2(THF)$	33.41	5.96	9.38	12.33	27.79		33.00	5.89	9.35	12.30	28.00				80–82
$AlHClI \cdot 2(THF)$	30.36	5.38	7.71	10.13		36.28	31.72	5.22	7.86	10.30		38.70			169–170
$AlD_2I \cdot 3(THF)$	38.52	7.53[a]	7.27			33.91	38.10	7.78	7.05			33.60			161–163

[a] Total hydrogen calculated for H and D. [b] Calculated for $AlH_2Cl \cdot 1.84(THF)$. [c] Mass spectral analysis showed an H/D ratio of 1.1 upon hydrolysis with water.

Discussion

The reaction of AlH_3 and the appropriate aluminum halide is the most general method for preparing bis(tetrahydrofuran)–haloalanes

$$AlH_3 + 2AlX_3 \xrightarrow{THF} 3AlHX_2 \cdot 2(THF)$$

$$2AlH_3 + AlX_3 \xrightarrow{THF} 3AlH_2X \cdot 2(THF)$$

Chloroalanes can also be prepared by the reaction of $LiAlH_4$ or $NaAlH_4$ with HCl, or $AlCl_3$ with $LiAlH_4$; the latter method has the advantage of giving well-formed crystals. Contrary to the observation of Ashby and Prather,[8] LiCl always precipitated when the reactions were carried out in diethyl ether. Differences in reaction temperature may account for the divergent results. Bromoalanes and iodoalanes can be prepared from AlH_3 and aluminum halide, although the most convenient preparation of $AlH_2I \cdot 2(THF)$ is the reaction of iodine solution and AlH_3. Iodoalanes are less soluble and higher melting than the chloro- and bromoalanes, which probably accounts for the ease of formation of the crystalline monoiodide. The formation of $AlD_2I \cdot 3(THF)$ was unexpected and merits further investigation.

Bis(diethyl ether)–haloalanes could not be prepared; however, the existence of stable bis(tetrahydrofuran) adducts was not surprising since $AlCl_3 \cdot 2(THF)$ has been reported.[9] Bis(tetrahydrofuran) adducts generally melted higher than the reported monotrimethylaminates[10] and triethylaminates,[8] which facilitated isolation and handling.

From the active hydrogen determinations of the chloro- and bromoalanes (Table I), it is apparent that no cleavage of THF has occurred and that the compounds exist as true adducts. The apparent molecular weights in benzene (Table II) are consistent with dissociation of the complex. The degree of dissociation of $AlHCl_2 \cdot 2(THF)$, $AlH_2Cl \cdot 2(THF)$, $AlHBr_2 \cdot 2(THF)$, and $AlH_2Br \cdot 2(THF)$ is 0.17, 0.16, 0.15, and 0.14, respectively, if THF and $AlH_yX_{3-y} \cdot (THF)$ are the products. This is consistent with the observation that the per cent of carbon diminishes when haloalane adducts are kept on a vacuum line for an extended period of time. Many analyses indicated 1.6–1.8 moles of THF in the product which suggests that one molecule of THF is relatively labile.

Molecular weights in THF solution indicate a monomeric species from which the dissociation of THF would not affect the apparent molecular weight. It has been reported that chloroalanes slowly cleave boiling THF;[11] however, the observed molecular weight should not change since the number of molecules in solution would remain the same.

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TABLE II

MOLECULAR WEIGHTS OF HALOALANE ADDUCTS

Compound	Mol wt		
	Calcd	Obsd[a]	Obsd[b]
$AlHCl_2 \cdot 2(THF)$	243	208	236
$AlDCl_2 \cdot 2(THF)$	244	. . .	247
$AlH_2Cl \cdot 2(THF)$	208	180	209
$AlHBr_2 \cdot 2(THF)$	332	288	331
$AlH_2Br \cdot 2(THF)$	252	221	237

[a] Cryoscopically in benzene (concentration range, 3–5 *M*). [b] Ebullioscopically in THF (concentration range, 0.02–0.04 *M*).

The X-ray powder pattern data given in Table III indicate the series of compounds are isotypic. Single-crystal X-ray studies are in progress to determine the lattice constants of $AlHCl_2 \cdot 2(THF)$ and $AlH_2Cl \cdot 2(THF)$.

Proton magnetic resonance spectra of chloro- and bromoalane adducts were obtained and the results are reported in Table IV. Hydride nuclei were not observed. Differences in proton shifts for $AlH_yX_{3-y} \cdot 2(THF)$ solution and THF solvent only indicate that THF remains complexed to a significant degree in $AlH_yX_{3-y} \cdot 2(THF)$ solutions. If an equilibrium exists between free and complexed THF, the equilibration must be very fast since a single THF pattern was observed in all cases. A comparison of the shifts in different solvents indicates significant solvent interaction by benzene, especially for $\beta(C–CH_2)$ protons. While shielding increases for β protons, $\alpha(O–CH_2)$ protons are apparently less shielded in the complexes. A small decrease in α proton shielding is observed when the number of halide substituents increases.

TABLE III

X-RAY POWDER DIFFRACTION DATA OF HALOALANE ADDUCTS

$AlH_2Cl \cdot 2(THF)$		$AlD_2Cl \cdot 2(THF)$		$AlHCl_2 \cdot 2(THF)$		$AlDCl_2 \cdot 2(THF)$		$AlH_2Br \cdot 2(THF)$		$AlHBr_2 \cdot 2(THF)$		$AlH_2I \cdot 2(THF)$		$AlHI_2 \cdot 2(THF)$		$AlHClBr \cdot 2(THF)$		$AlHClI \cdot 2(THF)$	
d, A	I/I_1	*d*, A	I/I_1	*d*, A	I/I_1	*d*, A	I/I_1	*d*, A	I/I_1	*d*, A	I/I_1	*d*, A	I/I_1	*d*, A	I/I_1	*d*, A	I/I_1	*d*, A	I/I_1
9.4	10	9.4	8	9.5	25	9.5	20	8.7	28	7.7	31	10.0	27	7.5	100	8.2	45	7.6	64
8.5	64	8.5	63	8.2	63	8.2	67	7.8	28	7.0	75	8.2	40	5.7	16	7.4	100	5.7	48
7.9	10	7.8	10	7.4	63	7.4	83	7.4	80	6.25	100	7.3	53	4.80	16	5.9	70	4.65	8
7.4	24	7.3	20	5.8	38	5.8	50	5.7	80	5.9	15	5.4	40	4.21	100	5.6	70	4.30	8
6.9	20	6.8	15	5.5	100	5.5	100	5.4	100	5.75	25	4.35	20	3.50	33	5.0	17	4.11	100
5.6	64	5.6	63	4.91	31	4.90	33	4.86	40	5.0	100	4.11	100			4.65	30	3.40	56
5.4	100	5.4	100	4.70	15	4.70	20	4.49	48	4.84	63					4.40	6	3.21	24
4.80	48	4.80	40	4.55	38	4.55	33	4.09	64	3.81	63					4.25	10		
4.40	64	4.40	50	4.35	20	4.35	13	3.82	16	3.59	63					4.10	35		
4.07	64	4.05	63	4.24	20	4.23	13			3.48	63					3.98	10		
3.80	16	3.79	13	4.10	38	4.09	33			3.23	17					3.60	10		
2.87	11	2.87	4							2.87	44					3.21	10		
2.67	3	2.67	1							2.80	10					2.90	6		
2.52	3	2.52	1							2.59	25					2.80	10		
2.41	5	2.41	2							2.51	20					2.45	6		
2.30	5	2.31	2							2.39	44					2.38	6		
2.20	5	2.20	2							2.33	31								
										2.18	15								
										2.11	10								
										2.05	15								

TABLE IV

PROTON MAGNETIC RESONANCE SHIFTS

Sample[a]	Concn of THF, *M*	Chem shift, ±0.01 ppm[b]		
		$\alpha(O–CH_2)$	$\beta(C–CH_2)$	Difference
$AlH_2Br \cdot 2(THF)$	1	−3.82	−1.33	2.49
$AlHBr_2 \cdot 2(THF)$	1	−3.85	−1.29	2.56
$AlH_2Cl \cdot 2(THF)$	1	−3.81	−1.30	2.51
$AlHCl_2 \cdot 2(THF)$	1	−3.84	−1.23	2.61
$AlHCl_2 \cdot 2(THF)$ in CCl_4	0.25	−4.16 ± 0.03	−2.02 ± 0.03	2.14
THF	0.32	−3.58	−1.44	2.14
THF	1.64	−3.58	−1.48	2.10
THF in $Si(CH_3)_4$ (TMS)	0.70	−3.62	−1.74	1.88
THF in CCl_4	0.94	−3.62	−1.79	1.83

[a] The solvent was benzene unless indicated otherwise. [b] Chemical shifts were taken as the position of the central peak of each proton type, and they are reported as shielding (ppm) relative to internal TMS. The benzene shift relative to TMS was assumed to be −7.17 ppm when no internal TMS was used. In general the limits of accuracy are ±0.01 ppm, except for $AlHCl_2 \cdot 2THF$, where the limits are ±0.03.

A tentative explanation of the observed data involves solvent and inductive effects. In CCl_4 solution, where solvent effects should be relatively small, complex formation causes deshielding at both α and β protons. The large shielding of protons, especially β, upon changing from CCl_4 to benzene solutions implies a specific orientation of the benzene ring π system toward THF molecules. The steric hindrance of other substituents reduces interaction of the solvent with α protons. The coordinate covalent bond between aluminum and oxygen atoms reduces the electron density at the oxygen nucleus and decreases shielding at adjacent hydrogen nuclei. Although the magnetic anisotropy of the complex can affect the net magnetic field at the THF protons, no estimate of the magnitude of this factor has been made. These data are consistent with a trigonal-bipyramid model (C_{2v}) having THF molecules at the apices, but they are clearly not definitive.

Infrared spectra of AlH_3 complexes have previously been interpreted in terms of the coordination number of the complex, the coordinating ligand, and the electronegativity of the substituents attached to the alum-

TABLE V

VIBRATIONAL FREQUENCIES OF Al–H IN $AlH_yX_{3-y}\cdot 2(THF)$ COMPLEXES[a]

Compound	Vibrational frequencies, cm^{-1}							
AlH_2Cl	1836 m	1755 s			805 vs	776 s, sh 712 s		
AlH_2Br	1842 w, sh	1772 s			807 s	776 m, sh 718 s		
AlH_2I		1782 m, sh 1737 s			800 w	737 m 722 m		
AlD_2Cl			1340 s 1300 vs				600 vs	559 s 528 s
AlD_2I[b]			1340 s, sh 1305 vs					597 vs 538 s 514 m
$AlDCl_2$			1338 s	1298 vs			600 vs	
$AlHCl_2$	1838 vs	1753 vs			803 s			
$AlHBr_2$	1848 vs	1761 s			803 s			
$AlHClBr$	1851 s	1765 s			812 s			
$AlHI_2$		1792 sh 1746 s				792 w		

[a] All bands are reported in cm^{-1} within an estimated error of ± 2 cm^{-1}. vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [b] Chemical analysis indicated $AlD_2I\cdot 3(THF)$.

inum atom[3,8,12,13] Four-coordinate aluminum has generally given a higher Al–H frequency than five- and six-coordinate aluminum. Increases in Al–H frequencies have been observed when electronegative elements are attached to the aluminum atom. The relative basicities and steric hindrance of coordinating ligands explain the frequency shifts associated with polymerization and hydrogen bridging in different solvents.

Vibrational frequencies for the hydrides are tabulated in Table V. The Al–H stretching frequencies appear in the 1700–1900-cm^{-1} region and the Al–D stretching frequencies in the 1200–1400-cm^{-1} region. Bending vibrations or deformations appear in the 850–700-cm^{-1} region for Al–H and 650–500 cm^{-1} for Al–D. Our data do not support hydrogen bridging in these THF complexes. Therefore, the splitting of the Al–H band in the 1700–1900-cm^{-1} region can be attributed to crystal splitting, site symmetry, or absence of band degeneracy because of low symmetry. When the monohydride THF complexes were dissolved in an excess of THF, a single band at lower frequency was normally observed. This can be attributed to the removal of site symmetry or simply to the increase of the coordination number to six.

The vibrational frequencies near 1840 cm^{-1} are lower than those reported for the four-coordinate $AlH_yX_{3-y}\cdot N(C_2H_5)_3$ complexes.[8] The reported frequencies could not be reproduced in this laboratory, although the observed frequency for $AlHCl_2\cdot N(C_2H_5)_3$ was higher than that of the corresponding THF complex. Al–H stretching frequencies were observed at 1866 and 1812 cm^{-1} for $AlHCl_2\cdot N(C_2H_5)_3$, and at 1835 and 1773 cm^{-1} for $AlH_2Cl\cdot N(C_2H_5)_3$. The reported values are 1897 cm^{-1} for $AlHCl_2\cdot N(C_2H_5)_3$ and 1852 cm^{-1} for $AlH_2Cl\cdot N(C_2H_5)_3$.

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The Shift of Ligand Stretching Frequencies upon Coordination with Special Reference to $SnCl_3^-$ Complexes

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We wish to report some interesting observations concerning the tin-chlorine stretching frequencies in complexes of $SnCl_3^-$ and a generalization relating to the internal vibration frequencies of σ-bonded ligands. In solution the free $SnCl_3^-$ ion is pyramidal and displays two Sn–Cl stretches at 297 and 256 cm^{-1}, respectively.[2] Furthermore, Raman polarization data show that the 297-cm^{-1} band arises from the totally symmetric mode.[2] In the infrared we observe these same two bands at 289 (ms) and 252 (s) cm^{-1} for mulls of solid $[(C_6H_5)_4As][SnCl_3]$. By contrast, the stretching frequencies of methyltrichlorostannane occur approximately 100 cm^{-1} higher; *viz.*, 366 and 384 cm^{-1}.[3] Thus,

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[1] (a) Northwestern University, Alfred P. Sloan Fellow, 1967–1969; (b) Union Carbide Corp.

[2] L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 407 (1962).

[3] P. Tainsula and J. L. Wood, *Spectrochim. Acta*, **20**, 1043 (1964).