This result is unexpected from the reported pK_2 values for the two acids, 1.7[16] for selenic acid and 1.98[17] for sulfuric acid.

Figure 2 is a plot of H_0 vs. water activity (determined from aqueous vapor pressure) for sulfuric,[15] perchloric,[11] and selenic acids.[18] All of these H_0 values have been obtained using primary aniline indicators. As can be seen the values for selenic acid fall on the curve described by the other two acids. Thus, all three acids at a particular water activity have the same proton donating ability. The values of Braun[12] for mixed

acetic acid–sulfuric acid have not been included in Figure 2 yet they do fall on the curve described by the other acids. These data serve to validate the water activity–H_0 correlation at high acidities.

Perrin[9] has pointed out that it is even possible to determine the H_0 of a mixed perchloric acid–salt solution from the water activity of the solution and a plot such as Figure 2.

One note of caution must be stated here. Those acids which are commonly referred to as weak acids may not fit the H_0–water activity relationship. It has been pointed out that phosphoric[4,12] acid and hydrofluoric[4] acid solutions do not fit on the curve shown in Figure 2.

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Structural Properties of Tetramethylammonium Tribromonickelate(II)[1]

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Abstract: The crystal structure of $(CH_3)_4NNiBr_3$ has been determined by three-dimensional, single-crystal, X-ray diffraction techniques. The structure consists of linear one-dimensional chains of nickel atoms bridged by three bromine atoms. The bromine atoms are not midway between the nickel atoms due to packing requirements of the $(CH_3)_4N^+$ ion, but are 2.45 and 2.67 A from the nickel atoms so that the site symmetry of the nickel atoms is C_{3v}. Lattice parameters and preliminary structural results are given for $CsNiBr_3$, $CsNiCl_3$, and $(CH_3)_4NNiCl_3$. The electronic absorption spectrum for $(CH_3)_4NNiBr_3$ is described and compared with that of $(CH_3)_4NNiCl_3$.

The different types of structures possible for octahedral complex halides of the type $R^IM^{II}X_3$, where R is an univalent cation, M a divalent metal, and X a halogen, have been discussed in detail by Wells.[2] The perovskite structure, in which octahedral edges are shared, is in general stable only for the more electronegative fluorides or oxides. The sharing of octahedral faces is rare, presumably because of the close approach of the metal atoms, and has been found almost always in complexes in which the metal atom has a formal oxidation number of three, e.g., $Cr_2Cl_9^{3-}$, $V_2Cl_9^{3-}$, $Ti_2Cl_9^{3-}$,[3] $Tl_2Cl_9^{3-}$,[4] and $ZrCl_3$.[5,6] The disputed $BaNi^{IV}O_3$ structure[7] is presumably also of this type. If an increase in the atomic radius of the metal atom is not a determining factor, a linear chain of $M^{II}X_3^-$ groups with three bridging halogen atoms might be expected since the anion to cation formal charge ratio of 1.5 is the same as in $M^{III}_2X_9^{3-}$ anions. Since Wells' review,[2]

when no structures with M^{II} were known, the only three-dimensional structural work has been with $CsCuCl_3$[8a,b] in which the Cu atoms form a nonlinear chain about a 6_1 axis with three copper–chlorine distances, 2.281, 2.355, and 2.776 A. This structure can be described as copper atoms sharing faces of their chlorine octahedra,[8a] or alternatively in view of the 0.5 A difference in copper–chlorine bond lengths as octahedra sharing edges.[8b] We wish to report here an X-ray study of a linear trihalogen bridged structure in which the metal atom has a formal oxidation number of two.

Experimental Section

$(CH_3)_4NNiBr_3$ was prepared by evaporating a 48.5% HBr solution containing 0.1 mole of $(CH_3)_4NBr$ and 0.1 mole of $NiBr_2\cdot6H_2O$. All compounds were reagent grade. The red-brown needle crystals had hexagonal cross sections and were assumed to be cylindrical for the absorption corrections described below. The crystals were somewhat hygroscopic and were sealed in thin-walled (0.01 mm) glass capillaries.

Anal. Calcd for $(CH_3)_4NNiBr_3$: Br, 64.3; Ni, 15.8; N, 3.8; C, 12.9; H, 3.2. Found: Br, 63.7; Ni, 15.1; N, 4.1; C, 14.3; H, 4.1.

A crystal with a diameter of approximately 0.10 mm and a length of 0.57 mm was used for collecting intensity data. Multiple-film equiinclination Weissenberg techniques were used to obtain

(1) This work supported in the initial stages by Petroleum Research Fund Starter Grant No. 232 and in part by the Advanced Research Projects Agency under Contract SD-131.
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Table I. Observed and Calculated Structure Factors (unobserved data are indicated by an asterisk)

L = 0

H	K	OBS	CAL
2	1	2.2	4.8*
3	1	58.5	53.9
4	1	67.8	78.6
5	1	15.3	13.6
6	1	8.7	7.3
7	1	10.1	10.6
8	1	3.5	3.0*
1	2	30.6	39.5
2	2	58.7	67.3
3	2	102.6	122.2
4	2	64.0	68.8
5	2	17.9	18.8
6	2	11.3	9.2
7	2	3.7	.4*
8	2	3.1	3.3*
0	3	10.7	14.5
1	3	16.6	10.5
2	3	58.8	60.2
3	3	76.7	81.9
4	3	22.8	20.8
5	3	8.1	2.6
6	3	15.0	14.4
7	3	18.1	15.5
8	3	2.4	5.3*
0	4	3.5	2.2*
1	4	7.6	3.9
2	4	18.5	18.2
3	4	10.4	8.8
4	4	3.9	.7*
5	4	10.4	9.0
6	4	27.5	24.5
1	5	17.2	15.7
2	5	3.7	3.6*
3	5	11.1	8.1
4	5	3.8	.8*
5	5	21.1	17.7
6	5	19.6	19.0
0	6	7.0	6.8
1	6	15.9	12.9
2	6	24.9	22.0
3	6	9.5	7.7
0	7	20.1	18.3
1	7	43.6	45.4
2	7	28.6	25.3
3	7	3.3	4.4*
0	8	29.8	26.6
1	8	29.2	28.4
2	8	13.3	13.5
0	9	14.2	13.6
1	9	10.7	7.9

L = 1

H	K	OBS	CAL
0	1	12.9	6.9
0	2	111.3	109.0
0	3	88.9	94.2
0	4	6.8	8.3
0	5	45.6	45.2
0	6	25.7	27.1
0	7	4.0	1.9
0	8	2.5	3.7*
0	9	5.3	5.4
1	1	19.7	21.8
1	2	105.0	97.8
1	3	56.9	51.9
1	4	50.5	47.9
1	5	66.5	56.9
1	6	13.4	15.6
1	7	1.5	.2*
1	8	2.3	1.2*
1	9	3.7	6.1
2	1	24.2	23.9
2	2	14.3	13.0
2	3	6.1	6.1
2	4	18.0	21.3
2	5	2.5	.7*
2	6	7.9	5.8
2	7	2.5	1.3*
2	8	2.0	1.3*
3	1	30.4	29.2
3	2	5.0	6.4
3	3	2.2	.6*
3	4	19.8	21.7
3	5	35.6	30.6
3	6	9.6	10.6
3	7	9.6	11.0
3	8	3.6	5.0
4	1	12.9	10.3
4	2	7.4	9.4
4	3	8.6	10.2
4	4	29.8	30.8
4	5	19.4	17.5
4	6	5.4	5.0
4	7	13.3	11.8
5	1	12.2	11.8
5	2	24.1	26.9
5	3	13.2	13.6
5	4	11.3	9.3
5	5	2.3	2.0*
6	1	26.4	30.1
6	2	31.1	28.1
6	3	11.5	11.6
7	1	19.2	17.7
7	2	11.4	10.3
8	0	2.5	3.7*
8	1	5.9	7.1
9	0	8.5	5.4
9	1	11.5	10.4

L = 2

H	K	OBS	CAL
0	1	25.7	29.2
0	2	81.3	74.5
0	3	84.6	77.5
0	4	54.9	47.0
0	5	50.5	43.0
0	6	33.1	30.2
0	7	8.5	8.9
0	8	9.0	6.6
0	9	2.0	3.3*
1	1	62.0	46.1
1	2	91.6	84.4
1	3	53.0	45.0
1	4	44.7	45.5
1	5	52.3	46.5
1	6	18.3	15.8
1	7	18.4	16.6
1	8	12.6	10.0
2	1	74.1	61.7
2	2	10.0	8.7
2	3	7.4	11.5
2	4	25.2	22.3
2	5	30.2	29.6
2	6	5.7	7.1
2	7	8.8	6.2
2	8	1.9	2.8*
3	1	11.3	11.7
3	2	53.7	58.9
3	3	30.7	27.0
3	4	25.6	23.3
3	5	29.8	30.1
3	6	12.0	13.5
3	7	10.0	10.4
4	1	16.8	18.1
4	2	22.2	23.8
4	3	16.3	13.0
4	4	27.3	27.3
4	5	20.1	18.9
4	6	11.7	14.6
4	7	8.9	10.6
5	1	23.5	22.1
5	2	20.1	18.4
5	3	23.3	25.8
5	4	12.0	11.5
5	5	2.2	2.4*
5	6	6.2	6.7
6	1	32.3	32.3
6	2	30.4	29.8
6	3	10.1	8.5
6	4	9.4	7.5
6	5	7.4	6.0
7	1	14.9	14.4
7	2	15.2	17.3
7	3	2.0	3.6*
7	4	6.0	5.9
8	1	11.1	12.8
8	2	9.9	11.0
9	1	9.8	11.7

L = 3

H	K	OBS	CAL
0	1	7.2	7.0
1	1	17.0	15.3
2	1	15.2	14.0
3	1	21.1	21.4
4	1	8.9	7.3
5	1	9.1	8.0
6	1	18.4	21.2
7	1	13.3	12.9
8	1	3.2	5.4
0	2	65.8	68.7
1	2	62.7	60.3
2	2	14.2	12.5
3	2	3.7	3.9
4	2	5.8	6.5
5	2	18.1	19.3
6	2	19.1	20.6
7	2	7.5	7.7
8	2	7.6	7.4
0	3	65.1	64.1
1	3	35.4	35.4
2	3	7.7	5.4
3	3	5.6	1.4
4	3	6.4	7.5
5	3	9.8	9.8
6	3	8.7	8.4
0	4	2.0	3.2*
1	4	28.8	31.8
2	4	14.5	14.1
3	4	13.0	14.9
4	4	19.1	21.7
5	4	8.4	7.2
0	5	33.0	31.7
1	5	38.6	40.8
2	5	2.3	1.3*
3	5	22.5	23.1
4	5	13.3	12.5
0	6	17.8	19.4
1	6	10.3	10.8
2	6	5.7	3.8
3	6	8.2	7.4
4	6	3.7	3.3
0	7	2.4	1.2*
1	7	2.2	.4*
2	7	2.0	1.1*
0	8	2.1	2.7*
0	9	3.9	3.8

411 *hkl* observed intensities of which 181 were independent with Ni-filtered Cu Kα radiation from *hk*0, *hk*1, *hk*2, and *hk*3 levels. In addition, *h0l* and *hhl* precession-timed exposure intensity data were collected with Zr-filtered Mo Kα radiation and used for preliminary scaling purposes. All intensities were visually estimated with a calibrated strip by two independent judgers and the set of judged intensities with the best internal consistency was used for the determination of the structure.

Calculations were made with an IBM 7094 computer. Lorentz, polarization, and cylindrical absorption corrections[9] reduced the observed intensities to squared structure factors. The linear absorption coefficient (μ) for this compound is 185.5 cm^{-1} with Cu Kα radiation. This gives a calculated value of 0.87 for μR for the crystal used. Fourier calculations were made with the Sly–Shoemaker–Van den Hende program. The full matrix, least-squares refinement was carried out using the Busing and Levy ORFLS program modified to make real and imaginary anomalous dispersion corrections. The necessary parameters used for the latter were those of Dauben and Templeton.[10] No corrections were made for extinction. The weighting scheme was based on

$$\sigma = 0.05F\left[\sqrt{10}\,\frac{I_{\min}}{I_{\text{obsd}}}\right]^2 \qquad I_{\text{obsd}} < \sqrt{10}I_{\min}$$

$$\sigma = 0.05F \qquad I_{\text{obsd}} \geq \sqrt{10}I_{\min}$$

with $\omega = 1/\sigma^2$. Unobserved reflections were assigned an intensity and weight according to Hamilton.[11] The function $\Sigma\omega(|F_o| - |F_c|)^2$ was minimized. Atomic scattering factors were taken from the compilation of Ibers for C, N, Ni, and Br.[12] The variables were scale factors, atomic coordinates, and individual atom temperature factors for isotropic refinement. One cycle of anisotropic refinement was carried out after the isotropic refinement was complete with scale factors fixed.

Transmission absorption spectra were measured with a Cary Model 14M recording spectrophotometer using a Nujol mull on filter paper.

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Results

Unit Cell and Space Group. (CH₃)₄NNiBr₃ crystallizes with two formula units per cell in the hexagonal crystal system. Unit cell constants were found to be $a = b = 9.35 \pm 0.02$ A, $c = 6.35 \pm 0.01$ A. The only systematic extinctions were 00*l*, $l = 2n + 1$. With the Laue symmetry 6/m, this implies the space group P6₃ or P6₃/m. Two formula units per cell require either $\bar{6}$ or $\bar{3}$ symmetry for the nitrogen atom in P6₃/m but only threefold symmetry in P6₃, so that the latter space group was initially assumed. The calculated density is 2.57 g cm^{-3} and the observed density was 2.49 g cm^{-3}.

Determination of the Structure. A three-dimensional Patterson map revealed the positions of the nickel and bromine atoms. The nickel atoms were taken at (0, 0, 0) and (0, 0, ¹/₂) in P6₃, fixing the origin. The bromines were then found in the general positions $(x, y, \frac{1}{4})$, etc. A three-dimensional electron density calculation with phases based on the Ni and Br positions gave the N and C positions. After seven cycles of isotropic least-squares refinement the disagreement index R ($R = \Sigma(||F_o| - |F_c||/\Sigma|F_o|)$) was 11.1% observed and unobserved reflections. For observed data only $R = 10.3\%$. A subsequent anisotropic cycle gave $R = 10.4\%$ for observed and unobserved data and 9.6% for observed data only. No significant positional parameters shifts occurred and all results quoted in this paper are based on the isotropic refinement. The maximum shift of positional coordinates for the last cycle was 0.0002 of the cell edges. The final calculated and observed structure factors are listed in Table I. Final atomic parameters and standard deviations are tabulated in Table II. Interatomic distances, angles, and errors are listed in Table III.

Description of the Structure. The structure consists of a linear chain of nickel atoms with site symmetry
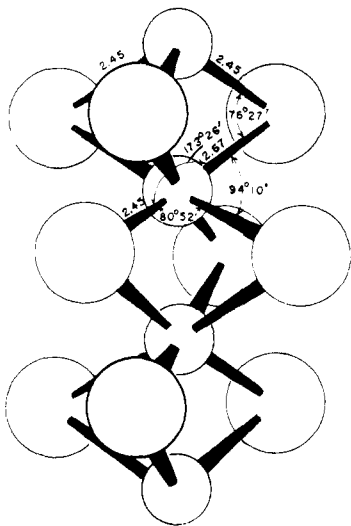
Figure 1. Nickel and bromine atoms in tetramethylammonium tribromonickelate(II).
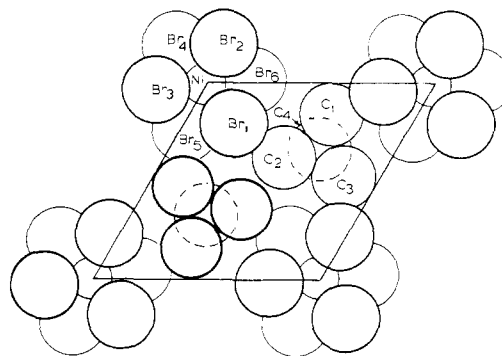

Figure 2. Unit cell of tetramethylammonium tribromonickelate-(II). The c axis is normal to the plane of the paper. The nitrogen atoms ($\frac{1}{3}$, $\frac{1}{3}$, 0.2556) have been omitted for clarity. In this projection C_4 and its symmetry equivalent (dashed atoms) are, respectively, beneath C_1, C_2, C_3, and their symmetry equivalents.

C_{3v} and Ni–Ni distance of 3.17 A. The $(CH_3)_4N^+$ groups are on threefold axes at $\frac{1}{3}$, $\frac{2}{3}$, 0.256 and impart a directional sense to the structure in that the inverted umbrellas formed by three carbon atoms of $(CH_3)_4N^+$ point in the same direction for all tetramethylammonium molecules. The observed displacements of the

Table II. Positional, Temperature, and Scale Parameters and Errors (numbers in parentheses are the estimated standard deviations in the least significant place)

Atom	x	y	z	B
Br	0.1466(3)	0.2461(4)	0.7794(29)	4.97(11)
Ni	0.0000	0.0000	0.0000	2.49(14)
C_1	0.1684(40)	0.6383(41)	0.3277(67)	5.36(75)
C_4	0.3333	0.6667	0.0153(84)	5.84(95)
N	0.3333	0.6667	0.2556(90)	2.31(46)

Layer	Scale factor
$hk0$	0.9095(27)
$hk1$	1.517(44)
$hk2$	1.477(46)
$hk3$	1.544(49)

Table III. Distances and Angles for $(CH_3)_4NNiBr_3{}^a$

⌐——— Bonded distances, A, and angles, deg ———⌐			
Ni–Br$_1$	2.67(1)	Br$_1$–Ni–Br$_4$	173.43(26)
Ni–Br$_6$	2.45(1)	Br$_1$–Ni–Br$_2$	80.86(26)
N–C$_1$	1.50(5)	Br$_1$–Ni–Br$_6$	94.17(27)
N–C$_4$	1.53(7)	Br$_4$–Ni–Br$_6$	90.45(28)
		Ni–Br$_4$Ni$_1$	76.45(19)
		C$_1$–N–C$_2$	111.1(2.60)
		C$_1$–N–C$_4$	107.7(2.09)

Nonbonded intermolecular distances, A			
Ni–Ni	3.17(1)	Br$_1$–C$_2$	3.73(3)
Br$_1$–Br$_2$	3.47(1)	C$_1$–C$_2$	2.47(6)
Br$_1$–Br$_6$	3.75(2)	C$_1$–C$_4$	2.44(7)
Br$_3$–C$_1$	3.74(3)		
Br$_4$–C$_1$	3.62(3)		
Br$_6$–C$_1$	4.01(4)		
Br$_3$–C$_3$	4.58(5)		
Br$_6$–C$_3$	4.00(4)		
Br$_6$–C$_4$	4.81(3)		

^{a} Refer to Figure 2. Br$_1$ is the Br position in Table II. Ni refers to the position (0, 0, $\frac{1}{2}$ and N to $\frac{1}{3}$, $\frac{1}{3}$, 0.2557).

bromine positions (0.1466, 0.2461, 0.7794) from the octahedral sites about the nickel atom (Figure 1) are consistent with optimizing the packing of the bromine atoms with the tetramethylammonium cation. Thus, the elongation of the Ni–Br$_1$ distance to 2.67 A places Br$_1$ 3.73 A from C$_4$ of the cation one unit cell in the [001] direction away from the labeled cation in Figure 2. This value (3.73 A) is representative of the other CH_3–Br distances in this structure. It should follow that monatomic cations such as Cs$^+$ and Rb$^+$ will give structures with NiX$_3{}^-$ anions in which the bridging halogens are exactly halfway between metal atoms. Unfortunately, there is considerable discrepancy in the literature concerning the only structure which has been examined, CsNiCl$_3$. Wyckoff[7] reports $a = 7.18$, $c = 17.79$ A. Tischenko,[13] on the basis of electron diffraction studies, gives the space group $P6_3/m$ mc (not isomorphous with CsCuCl$_3$ as reported by Schlueter, et al.[8]) with $a = 7.18$ and $c = 5.93$ A. Finally, Asmussen and Soling[14] report $a = 7.17$ and $c = 11.87$ A. From our X-ray data for CsNiCl$_3$ we find $a = 7.18$, $c = 5.93$ A, space group $P6_3/m$ mc in agreement with the parameters of Tischenko. This implies that the chlorines are indeed midway between the nickel atoms. CsNiBr$_3$ is isomorphous with CsNiCl$_3$, $a = 7.50 \pm 0.02$, $c = 6.24 \pm 0.01$ A, mol wt 431.34. The nickel-nickel distances are accordingly 2.97 and 3.12 A in the two compounds. Our preliminary structural data for CsNiBr$_3$ indicate a relatively short Br–Br distance of 3.50 A and a Ni–Br distance of 2.56 A. It is interesting to note that the latter value is almost exactly the average value of the two nickel–bromine distances in $(CH_3)_4NNiBr_3$.

Discussion

The RMX$_3$ compounds and the fact that single crystals can be obtained from these compounds offer the possibility of experimentally studying the relation of magnetic to structural properties in one of the simplest systems possible in which collective magnetic phenomena are found, namely the periodic infinite linear chain. Single crystals have not been previously grown of compounds such as ZrCl$_3$, and in addition in ZrCl$_3$,

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(14) R. W. Asmussen and H. Soling, Z. Anorg. Allgem. Chem., 283, 3 (1956).

CuCl₂, and CrCl₂ it is to be expected that interactions between chains are more likely to be a factor, thus adding another dimension to the problem.

The magnetic susceptibilities of several of the RMX_3 complexes have been measured to liquid nitrogen temperatures by Asmussen and Soling[14] and some of their data are reproduced in Table IV. Inasmuch as the Curie–Weiss constant increases[14] with the metal–metal distance as one goes from $CsNiCl_3$ to $CsNiBr_3$, indicating larger antiferromagnetic interactions, it would appear that in agreement with the discussion of Schlueter, et al.,[8] the important factor is not the metal–metal overlap. Stout and Chisholm[15] have pointed out that in the interlinked chain structures of $CuCl_2$ and $CrCl_2$ one would expect Kramers[16] superexchange to be much greater within the chain than between chains and were able to explain the heat capacity maximum (23.91 °K for $CuCl_2$) and magnetic susceptibility maximum (70 °K for $CuCl_2$) on this basis using an Ising model. The antiferromagnetic ordering in $CrCl_2$ within a chain has been verified by neutron diffraction studies.[17] Since exchange via the bridging halogens depends rather critically on the metal–halogen distance, the differences in the magnetic properties of tetramethylammonium[18] ($\theta = 0 °K$) and cesium[14] ($\theta = -75 °K$) salts of $NiCl_3^-$ might be explained to a large extent by distortions of the type found in tetramethylammonium tribromonickelate. We are currently examining the crystal structures and magnetic properties of several MX_3^- salts with different cations and transition metals to further correlate the magnetic and structural properties of these compounds. Neutron diffraction studies are being carried out at Argonne National Laboratories.

Table IV. Magnetic and Structural Data for $RNiX_3$ Compounds

Compound	Curie–Weiss constant $-\theta$, °K	Ref	μ_{eff}	Ni–Ni distance, A
$RbNiCl_3$	112	14	2.95; 20°	...
$CsNiCl_3$	76	14	3.01; 21°	2.97
$RbNiBr_3$	156	14	2.84; 21°	3.09
$CsNiBr_3$	101	14	2.94; 22°	3.12
$(CH_3)_4NNiCl_3$	0	a	3.20; 20°	3.08

ᵃ D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964).

The absorption spectra of some of the compounds $MNiX_3$ have been reported by Asmussen,[19] Cotton,[20] and Goodgame.[18] The absorption spectrum of $(CH_3)_4$-$NNiBr_3$ shows the following spin-allowed bands: $^3A_{2g} \rightarrow {}^3T_{2g}$ at 6300 cm⁻¹, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ at 10,400 cm⁻¹, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ at 19,700 cm⁻¹. In addition the following spin-forbidden bands are observed: $^3A_{2g} \rightarrow {}^1E_g(^1D)$ at ~11,400 cm⁻¹ and $^3A_{2g} \rightarrow {}^1T_{2g}(^1D)$ at 17,500 cm⁻¹ (s). There is no evidence of the trigonal distortion in the absorption spectra. Using the same method as Goodgame,[18] the value of Δ is 6300 cm⁻¹ and B' is approximately 750 cm⁻¹. Goodgame reports values of Δ and B' as 6600 and 840 cm⁻¹, respectively, for $(CH_3)_4NNiCl_3$. Preliminary X-ray data show that $(CH_3)_4NNiCl_3$, $a = 7.85$, $c = 6.16$ A, has a similar structure to that of $(CH_3)_4NNiBr_3$, but is not isomorphous; for example, using the same fractional position coordinates found in $(CH_3)_4NNiBr_3$ with the above experimental lattice parameters for $(CH_3)_4NNiCl_3$ results in a N–C distance of 1.22 A. The complete three-dimensional structure of this compound will be reported in a subsequent paper.

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Amination and Transamination as Routes to Fourth Group Diamines[1]

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Abstract: Preparation and properties of some examples of *gem*-diamines of carbon, silicon, germanium, and tin are presented. These bis(dialkylamino) compounds were used in transamination reactions with N,N'-disubstituted ethylenediamines to yield monomeric imidazolidine derivatives, with piperazine to yield analogs of 1,4-diazabicyclo-[2.2.1]heptane (germanium) or its dimer (silicon) and polymers, and with ethylenediamine to yield polymers. Backbone structures for the polymers are assigned on the basis of nmr and infrared spectra and analytical data. Mechanistic implications of the observed group IV reactivities toward amination (Si > Ge > Sn) and transamination (Sn > Ge > Si) are discussed.

This publication reports the results of our investigations on the synthesis and relative reactivities of organometallic diamines of carbon, silicon, germanium,

and tin. We were interested in the comparative aspects of the chemistry of the *gem*-diamines of these elements, especially the dialkyldiamines of the type