Triethanolamine Complexes of H^+, Li^+, Na^+, Sr^{2+}, and Ba^{2+} Perchlorates

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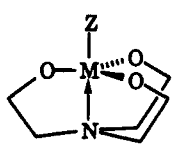
Received August 19, 1993®

The syntheses of the perchlorate salts of $H(TEA)^+$ (**1**), $Li(TEA)^+$ (**2**), $Na(TEA)^+$ (**3**), $Sr(TEA)_2^{2+}$ (**4**), and $Ba(TEA)_2^{2+}$ (**5**), wherein TEA = triethanolamine, are reported. Characterizational NMR spectral results (^1H, ^{13}C, ^7Li, ^{23}Na) as well as crystal structures for **1**, **3**, and **5** are discussed. The structures of **1**, **3**, and **5** reveal respectively the cation $H(TEA)^+$ in which the proton is in a tetrahedral environment, a seven-coordinate sodium weakly coordinated by a monodentate ClO_4^- and two OH oxygens from neighboring units, and a $[Ba(TEA)ClO_4]_2^{2+}$ cation in which two weakly coordinating perchlorates bridge two Ba^{2+} ions in a bidentate fashion. Extensive hydrogen bridging via ClO_4^- ions occurs in all three compounds giving rise to parallel sheet structures. Crystal data: **1** (at 22 °C), a = 9.086(1) Å and c = 23.919(6) Å, with Z = 6 in space group $R3c$; **3** (at 20 °C), a = 9.617(1) Å, b = 7.787(1) Å, c = 15.914(2) Å, and β = 105.80°, with Z = 4 in space group $P2_1/c$; **5** (at -50 °C), a = 7.498(2) Å, b = 10.492(2) Å, c = 15.749(3) Å, α = 76.06(2)°, β = 80.56(2)°, and γ = 76.70(2)°, with Z = 2 in space group $P\bar{1}$.

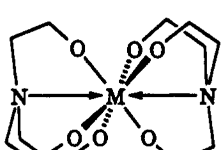
Introduction

The convenient synthesis of precursors for the formation of materials via sol-gel[1] or low-temperature MOCVD techniques[2] is an area of substantial interest. While conventional metal alkoxides of the type $M(OR)_x$ have been widely investigated for this purpose, much less emphasis thus far has been placed on such compounds derived from polyfunctional alcohols.

Triethanolamine (TEA) possesses advantages that render it worthy of study. Because of its chelating ability, it tends to form robust monomeric tricyclic ("atrane") structures of type **A** that



A



B

are easily solvolyzable and in many cases are also volatile at relatively low temperatures.[3] This is particularly true when M is metalloidal and when ZM = Ph_3SiOTi or O=V.[3b] Another advantage of TEA is that it is commercially available and relatively inexpensive.

Because of their low oxidation states, metals from groups 1 and 2 are unable to form structures of type **A**. Thus far, structural information on alkoxides formed from these metals and TEA has been restricted to one report, namely, that concerning the configuration of $Ba[(OCH_2CH_2)(HOCH_2CH_2)_2N]_2\cdot 2EtOH$,[4] in which Ba is octacoordinated by two TEA^- moieties in monomeric charge-neutral units that are connected in a two-dimensional network by hydrogen bonding with the ethanol molecules. The metal–oxygen–carbon–nitrogen framework for this complex is shown in **B**. Cationic coordination complexes of group 2 metals with TEA also tend to exhibit extensive hydrogen bonding via the anions,[5–10] which in some cases also coordinate to the metal, thus distorting structure **B** (as in nine-coordinate $[Ba(TEA)_2(2,4\text{-}(O_2N)_2C_6H_3O)](2,4\text{-}(O_2N)_2C_6H_3O)$,[5] ten-coordinate $[Ba(TEA)_2(\text{picrate})](\text{picrate})$,[6] nine-coordinate $[Ba(TEA)_2(OAc)]OAc$,[7] and ten-coordinate $[Ba(TEA)_2(OC_6H_4\text{-}o\text{-}NO_2)_2]$[8]) while in others framework **B** is preserved (i.e., eight-coordinate $[M(TEA)_2](\text{anion})_2$ (M = Ca, anion = N_3^-;[9] M = Sr, anion = N_3^-,[9] NO_3^- [10])). Except for $[Ba(TEA)_2(OC_6H_4\text{-}o\text{-}NO_2)_2]$, in which eight of ten oxygens are coordinated to two Ba^{2+} ions, giving rise to a complicated two-dimensional network of Ba–O interactions, the OH groups of ligating TEA have been found to coordinate to a single M^{2+} ion (structure **B**).

The only structural report of a group 1 metal–TEA complex is that for Na(TEA)I, wherein the sodium ion is seven-coordinate.[11] Thus, in addition to TEA and iodide coordination, two OH groups from each molecule bridge two Na^+ ions. The structure of uncomplexed TEA is also interesting in that it forms a dimer in the solid state in which all the OH hydrogens of each TEA hydrogen-bond to the arms of the other TEA molecule, forming a large discrete cage.[12] The six hydrogen bonds form a twelve-membered puckered ring around the "equator" of the cage, and the nitrogen lone pairs are clearly directed inwardly toward one another.

Here we report on synthesis of the perchlorate salts of $H(TEA)^+$ (**1**), $Li(TEA)^+$ (**2**), $Na(TEA)^+$ (**3**), $Sr(TEA)_2^{2+}$ (**4**), and $Ba(TEA)_2^{2+}$ (**5**). Compounds **1**, **3**, and **5**, which have been examined by X-ray crystallography, display novel structural features which are discussed.

Experimental Section

Warning! Although no difficulties were encountered with the syntheses or isolation of the perchlorate compounds discussed herein, appropriate precautionary measures should be taken.

General Procedures. All reactions were carried out under an atmosphere of argon at room temperature by using standard inert-atmosphere

® Abstract published in *Advance ACS Abstracts,* March 15, 1994.

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0020-1669/94/1333-2137$04.50/0

and Schlenk techniques,[13] unless otherwise stated. Tetrahydrofuran (THF), benzene, and Et_2O were distilled from Na/benzophenone under N_2. Triethanolamine (TEA) was distilled under vacuum and stored over 4-Å molecular sieves. Acetonitrile was distilled from CaH_2.

^1H and ^{13}C NMR spectra were recorded on a Nicolet NT-300 or a Varian VXR-300 instrument. FAB-MS spectra were obtained on a Kratos MS 50 instrument. ^7Li and ^{23}Na solid-state MAS NMR spectra were measured on a Bruker MSL 300 instrument and were referenced to an aqueous solution of LiCl and solid NaCl, respectively. ^7Li solution NMR chemical shifts were referenced to $LiClO_4$ in methanol-d_4 or acetonitrile-d_3 at δ −0.54 and −2.80, respectively. FT-IR spectra were recorded on an IBM-IR-98 spectrometer using KBr pellets or Nujol mulls. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. $LiClO_4$, $NaClO_4$, and $Ba(ClO_4)_2$ were purchased from Aldrich Chemical Co. $Sr(ClO_4)\cdot 6H_2O$ was purchased from Strem Chemical Co. and used without further purification. Silatranium perchlorate was prepared according to a procedure we describe elsewhere.[14]

H(TEA)ClO$_4$ (1). A 0.355-g quantity of a 70% solution of $HClO_4$ (2.47 mmol) was diluted in 50 mL of distilled H_2O. To this was added 0.33 mL (3.70 g, 2.48 mmol) of TEA dropwise at 0 °C. After the reaction mixture reached room temperature, stirring was continued for 18 h. The water was removed on a rotatory evaporator to obtain a slightly yellowish oil. The oil was dissolved in 15 mL of acetone, and then 5 mL of hexane was added. The mixture was cooled to −20 °C for 24 h to give small colorless crystals. After separation by decantation and washing with hexane, the crystals were dried under vacuum. The supernatant liquid was cooled at −20 °C for several days to give a second crop of crystals. Yield: 55%. ^1H NMR (acetone-d_6): δ 3.96 (t, 6 H, OCH_2, $^3J_{HH}$ = 5.1 Hz), 3.84 (s, 4 H, OH and *H*(TEA)), 3.53 (t, 6 H, NCH_2, $^3J_{HH}$ = 5.1 Hz). ^{13}C NMR (acetone-d_6): δ 56.53 (OCH_2), 56.31 (NCH_2).

Crystals of X-ray quality were accidentally obtained during an attempt to recrystallize a 0.36 M solution of $[Me_3C{\equiv}NSi(OCH_2CH_3)N]ClO_4$ from pivalonitrile.[14] Five milliliters of the clear solution in a small test tube was placed in a second large test tube containing CH_2Cl_2, which was then closed with a septum. Within a few days, crystals suitable for a crystallographic analysis grew in the inner test tube.

Li(TEA)ClO$_4$ (2). Lithium perchlorate (0.93 g, 8.7 mmol) and TEA (1.30 g, 8.70 mmol) were dissolved in a mixture of 15 mL of CH_2Cl_2 and 2 mL of THF. The yield of 46% of a white crystalline solid was obtained by slow evaporation of the solvents through a needle which was inserted into the septum on the vessel. Mp: 179–181 °C. ^1H NMR (acetonitrile-d_3): 3.97 (s, 3 H, OH), 3.61 (t, 6 H, OCH_2, $^3J_{HH}$ = 5.3 Hz), 2.61 (t, 6 H, NCH_2, $^3J_{HH}$ = 5.3 Hz). ^{13}C NMR (acetonitrile-d_3): δ 58.7 (OCH_2), 53.4 (NCH_2). ^7Li NMR (acetonitrile-d_3): δ −1.05. ^7Li (methanol-d_4): δ −0.35. ^7Li MAS NMR (3020 Hz): δ 0.1 ($\Delta\nu_{1/2}$ = 80 Hz). MS-FAB, *m/e* (relative intensity, ion): 156 (100, Li(TEA)$^+$). IR (KBr), cm^{-1}: 3523 vs, 3393 w, 3356 w, 3284 s, 3181 w, 3087 s, 2971 s, 2931 m, 2897 vs, 2850 s, 1484 m, 1453 w, 1423 w, 1401 w, 1376 s, 1312 s, 1278 m, 1225 m, 1135 vs, 1096 vs, 1065 vs, 1038 vs, 1012 s, 934 vw, 913 w, 887 vs, 857 w, 752 w, 627 vs, 537 s.

Na(TEA)ClO$_4$ (3). Sodium perchlorate (1.34 g, 10.9 mmol) and triethanolamine (1.63 g, 10.9 mmol) were dissolved in 10 mL of THF. Colorless crystals suitable for X-ray diffraction were grown by slow evaporation of the solvent through a needle which was inserted into the septum on the vessel. Yield: 34%. Mp: 129–130 °C. ^1H NMR (acetonitrile-d_3): δ 3.36 (s, 3 H, OH), 3.58 (t, 6 H, OCH_2, $^3J_{HH}$ = 5.1 Hz), 2.54 (t, 6 H, NCH_2, $^3J_{HH}$ = 5.1 Hz). ^{13}C NMR (acetonitrile-d_3): δ 59.2 (OCH_2), 56.3 (NCH_2). ^{23}Na MAS NMR (4069 Hz): δ −14 ($\Delta\nu_{1/2}$ = 850 Hz). MS-FAB, *m/e* (relative intensity, ion): 172 (100, Na(TEA)$^+$), 150 (10, TEA + H$^+$), 118 (11, TEA − CH_2OH). IR (KBr), cm^{-1}: 3513 vs, 3366 vw, 3264 m, 2980 s, 2895 s, 2828 s, 2738 w, 1478 w, 1457 w, 1405 w, 1378 m, 1317 m, 1280 vw, 1264 w, 1245 w, 1218 w, 1130 sh, 1110 vs, 1081 vs, 1035 s, 1017 w, 933 w, 907 m, 890 s, 737 w, 631 s, 566 m, 527 m. Anal. Calcd for $C_6H_{15}ClNNaO_7$: C, 26.53; H, 5.57; N, 5.16. Found: C, 26.73; H, 5.86; N, 5.11

Sr(TEA)$_2$(ClO$_4$)$_2$ (4). TEA (2.80 g, 19.7 mmol) was added dropwise to a methanol solution of 3.94 g (10 mmol) of $Sr(ClO_4)_2\cdot 6H_2O$. The reaction mixture was stirred at room temperature for 6 h, after which all the solvent was removed using a rotatory evaporator to obtain a mixture of solid and an oil. To this mixture was added about 30 mL of *i*-PrOH and 100 mL of Et_2O, and then the mixture was stirred for $^1/_2$ h. The solid was filtered off, washed with 200 mL of ether, and dried under vacuum to give a 46% yield of the final product. Mp: 205–210 °C dec. ^1H NMR (D_2O): δ 4.67 (s, 6 H, OH), 3.51 (t, 12 H, OCH_2, $^3J_{HH}$ = 6.0 Hz), 2.57 (t, 12 H, NCH_2, $^3J_{HH}$ = 6.0 H). ^{13}C NMR (D_2O, MeOH as external reference): δ 58.87 (OCH_2), 55.75 (NCH_2). MS-FAB, *m/e* (relative intensity, ion): 193 (10, Sr(TEA)$_2$/2), 150 (100, TEA + 1). IR (Nujol), cm^{-1}: 3349 s, 3312 m, 3211 m, 2952 s, 2292 s, 2852 w, 1456 m, 1142 m, 1092 m, 721 m, 630 w.

[Ba(TEA)$_2$(ClO$_4$)]$_2$ (5). $Ba(ClO_4)_2$ (1.68 g, 5.00 mmol) was dissolved in 40 mL of acetonitrile. To that mixture was added 1.49 g (10.0 mmol) of TEA. The reaction mixture was stirred overnight and then layered with Et_2O. Small colorless crystals grew in 98% yield after 5 h at 5 °C. Mp: 226–228 °C. ^1H NMR (acetonitrile-d_3): δ 4.05 (s, 12 H, OH), 3.70 (t, 24 H, $^3J_{HH}$ = 5.1 Hz, OCH_2), 2.55 (t, 24 H, $^3J_{HH}$ = 5.1 Hz, NCH_2). ^{13}C NMR (acetonitrile-d_3): δ 59.9 (OCH_2), 56.7 (NCH_2). MS-FAB, *m/e* (relative intensity, ion): 535 (42, [Ba(TEA)$_2$ClO$_4$]$^+$), 471 (2, [Ba(TEA)ClO$_4$]$^+$ − C_2H_4OH), 386 (100, [Ba(TEA)(OC$_2$H$_5$)-ClO$_4$]$^+$), 286 (69, [Ba(TEAH$^+$)]), 237 (17, Ba(ClO$_4$)$^+$). IR (Nujol), cm^{-1}: ν 3480 vs, 3432 s, 2753 s, 2921 vs, 2739 w, 2343 w, 2039 m, 1488 m, 1320 m, 1109 s, 1015 s, 895 m, 860 w, 801 w, 736 w, 620 m. Anal. Calcd for $C_{12}H_{30}BaCl_2N_2O_{14}$: C, 22.71; H, 4.77; N, 4.46. Found: C, 23.34; H, 4.93; N, 4.51.

NMR Data for Triethanolamine (TEA). ^1H NMR (acetonitrile-d_3): δ 3.60 (s, 3 H, OH), 3.50 (t, 6 H, OCH_2, $^3J_{HH}$ = 5.3 Hz), 2.59 (t, 6 H, NCH_2, $^3J_{HH}$ = 5.3 Hz). ^{13}C NMR (acetonitrile-d_3): δ 60.41 (OCH_2), 57.77 (NCH_2). ^1H NMR (acetone-d_6): δ 3.83 (s, 3 H, OH), 3.53 (t, 6 H, OCH_2, $^3J_{HH}$ = 5.4 Hz), 2.64 (t, 6 H, NCH_2, $^3J_{HH}$ = 5.4 Hz). ^{13}C NMR (acetone-d_6): δ 60.28 (OCH_2), 57.95 (NCH_2). ^1H NMR (D_2O): δ 4.67 (s, 3 H, OH), 3.52 (t, 6 H, OCH_2, $^3J_{HH}$ = 5.4 Hz), 2.57 (t, 6 H, NCH_2, $^3J_{HH}$ = 5.4 Hz). ^{13}C (D_2O, MeOH used as external reference): δ 58.62 (OCH_2), 55.40 (NCH_2).

Crystals suitable for X-ray study were obtianed by allowing a refluxing mixture of acetonitrile/benzene in a 5:1 ratio to cool to room temperature.

X-ray Structure Determinations of 1, 3, and 5. Colorless crystals of **1**, **3**, and **5** were mounted in glass capillaries inside an argon-filled glovebag. The measurements for 1 and 3 were made on an Enraf-Nonius CAD4 while those for 5 were obtained on a Siemens P4/RA diffractometer.

Pertinent data collection and reduction information are given in Table 1. Positional parameters and their estimated standard deviation for **1**, **3**, and **5** are collected in Tables 2–4, respectively. Selected bond distances and angles for 1, 3, and 5 are given in Tables 5–7, respectively.

All three structures were solved by direct methods.[15] Refinement calculations for 1 and 3 were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP program[16] while those for 5 were done on a Digital Equipment Corp. Micro VAX 3100/76 computer using the SHELXTL-Plus program.[17]

Table 1. Crystallographic Data for **1**, **3**, and **5**

	1	3	5
formula	$C_6H_{16}ClNO_7$	$C_6H_{15}ClNNaO_7$	$C_{12}H_{30}BaCl_2N_2O_{14}$
fw	249.61	271.63	634.6
space group	$R3c$	$P2_1/c$	$P\bar{1}$
a, Å	9.086(1)	9.617(1)	7.498(2)
b, Å	9.086(1)	7.787(1)	10.492(2)
c, Å	23.919(6)	15.914(2)	15.749(3)
α, deg	90.0	90.0	76.06(2)
β, deg	90.0	105.80(2)	80.56(2)
γ, deg	120.0	90.0	76.70(2)
V, Å^3	1710.1(9)	1146.7(5)	1162.5(4)
Z	6	4	2
μ(Mo Kα), mm^{-1}	3.57	3.9	2.006
data collec instr	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Siemens P4/RA
temp, °C	22(1)	20(1)	−50
R^a	0.024	0.033	0.029
$R_w{}^b$	0.031	0.050	0.038

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

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(17) SHELXTL-PLUS, Siemens Analytical X-Ray, Inc., Madison, WI.

Table 2. Positional Parameters and Their Estimated Standard Deviations for H(TEA)ClO$_4$ (**1**)

atom	x	y	z	B(eq), Å^2
Cl	1.000	1.000	0.582	3.97(1)
O1	0.8312(3)	0.9319(3)	0.6022(1)	7.13(6)
O2	1.000	1.000	0.5219(2)	7.78(7)
N	0.333	0.667	0.4326(1)	3.63(5)
C1	0.4993(3)	0.8162(4)	0.4145(1)	4.66(6)
C2	0.6396(3)	0.8422(3)	0.4529(1)	5.03(7)
O3	0.5899(2)	0.8644(3)	0.50670(9)	6.63(5)
H1	0.333	0.667	0.471(2)	0.9(7)
H2	0.646(4)	0.874(4)	0.534(1)	4.4(7)
H3	0.489	0.915	0.415	1.6(5)
H4	0.525	0.796	0.378	4.1(7)
H5	0.743	0.940	0.442	4.6(7)
H6	0.654	0.746	0.452	4.7(8)

Table 3. Positional Parameters and Their Estimated Standard Deviations for Na(TEA)ClO$_4$ (**3**)

atom	x	y	z	B(eq), Å^2
Na	0.96909(8)	0.3200(1)	0.24857(5)	3.11(2)
N	0.6892(2)	0.3072(2)	0.1831(1)	2.69(3)
C1	0.6585(2)	0.1350(3)	0.1441(2)	3.46(5)
C2	0.7623(3)	0.0822(3)	0.0936(2)	3.71(5)
O1	0.9021(2)	0.0566(2)	0.15256(9)	3.49(3)
C3	0.6226(2)	0.3330(3)	0.2551(1)	3.64(5)
C4	0.7028(3)	0.2478(4)	0.3377(2)	4.31(5)
O2	0.8485(2)	0.3046(3)	0.3600(1)	4.65(4)
C5	0.6400(2)	0.4425(3)	0.1170(1)	3.32(4)
C6	0.7147(3)	0.6117(3)	0.1449(2)	3.75(5)
O3	0.8677(2)	0.5989(2)	0.16203(9)	3.74(3)
Cl	1.16456(5)	0.29888(7)	0.07667(3)	3.29(1)
O4	1.0573(2)	0.1818(2)	0.0291(1)	4.66(4)
O5	1.1335(2)	0.3500(3)	0.1548(1)	6.36(4)
O6	1.2997(2)	0.2186(4)	0.0967(2)	8.81(7)
O7	1.1692(3)	0.4458(3)	0.0246(1)	7.22(6)

Table 4. Positional Parameters and Their Estimated Standard Deviations for [Ba(TEA)$_2$ClO$_4$]$_2$(ClO$_4$)$_2$ (**5**)

atom	x	y	z	B(eq), Å^2
Ba	0.00580(3)	0.21742(2)	0.78710(1)	2.36(1)
N	−0.0922(4)	0.0426(3)	0.6798(2)	2.6(1)
C1	0.0702(8)	−0.0076(6)	0.6217(4)	5.2(2)
C2	0.2480(7)	−0.0292(5)	0.6569(3)	4.1(1)
O1	0.2777(4)	0.0876(4)	0.6768(2)	4.1(1)
C3	−0.2387(10)	0.1218(5)	0.6253(4)	5.7(2)
C4	−0.2235(8)	0.2544(5)	0.5816(4)	4.9(1)
O2	−0.1812(6)	0.3258(3)	0.6385(2)	5.3(1)
C5	−0.1583(10)	−0.0651(6)	0.7430(3)	5.6(2)
C6	−0.2973(8)	−0.0325(5)	0.8135(3)	4.5(1)
O3	−0.2727(5)	0.0755(3)	0.8466(2)	3.9(1)
N′	0.1084(4)	0.4664(3)	0.8201(2)	2.3(1)
C1′	0.1700(7)	0.4255(4)	0.9091(3)	3.6(1)
C2′	0.3197(6)	0.3049(4)	0.9216(3)	3.6(1)
O1′	0.2763(5)	0.2012(3)	0.8895(2)	4.0(1)
C3′	0.2560(7)	0.5065(5)	0.7532(3)	4.0(1)
C4′	0.2258(7)	0.5132(5)	0.6614(3)	4.2(2)
O2′	0.1870(6)	0.3913(4)	0.6554(2)	5.3(1)
C5′	−0.0546(7)	0.5744(4)	0.8199(3)	3.9(1)
C6′	−0.2313(6)	0.5302(5)	0.8524(3)	3.9(1)
O3′	−0.2657(4)	0.4450(3)	0.8015(2)	3.6(1)
Cl1	0.2455(1)	−0.1475(1)	0.9474(1)	2.62(2)
O11	0.1300(6)	−0.547(3)	0.8889(3)	6.0(1)
O12	0.3511(6)	−0.2478(4)	0.9048(3)	6.6(1)
O13	0.1418(6)	−0.2067(4)	1.0237(2)	6.4(1)
O14	0.3664(4)	−0.0764(3)	0.9732(2)	3.3(1)
Cl2	0.2998(1)	0.3030(1)	0.4332(1)	2.66(2)
O21	0.1871(7)	0.4114(4)	0.4692(2)	6.3(1)
O22	0.1843(7)	0.2254(5)	0.4180(3)	6.8(2)
O23	0.3991(5)	0.3520(4)	0.3517(2)	5.4(1)
O24	0.4175(5)	0.2216(4)	0.4950(2)	6.0(1)

The data for the crystal of **5** were originally collected with copper radiation. The standard reflections gained intensity by 40% during the first 15 h of data collection but were essentially constant thereafter. This effect may be attributed to secondary extinction. After this point, usable data were collected using molybdenum radiation.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**

	Bond Lengths		
H1–O3	2.28(2)	Cl–O1	1.421(3)
H1–N	0.92(6)	Cl–O2	1.437(5)
	Bond Angles		
O3–H1–O3	107.0(2)	H1–N–C1	106.8(2)
O3–H1–N	112.0(1)	C1–N–C1	112.0(1)
H1–O3–C2	121.0(4)	O1–Cl–O2	109.8(1)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **3**

	Bond Lengths		
Na–N	2.611(2)	Na–O1a	2.518(2)
Na–O1	2.534(2)	Cl–O4	1.430(2)
Na–O2	2.372(2)	Cl–O5	1.412(2)
Na–O3	2.614(2)	Cl–O6	1.398(2)
Na–O5	2.463(2)	Cl–O7	1.420(2)
Na–O3a	2.497(2)		
	Bond Angles		
N–Na–O1	70.32(6)	C3–N–C5	109.6(2)
N–Na–O2	68.62(6)	Na–O1–C2	108.8(1)
N–Na–O3	68.00(6)	O4–Cl–O5	110.5(1)
N–Na–O5	121.60(8)	O4–Cl–O6	109.1(2)
O1–Na–O2	108.32(7)	Na–O5–Cl	146.2(1)
O1–Na–O5	79.10(6)	O1–Na–O1a	165.91(4)
N–Na–O1	123.75(6)	O1–Na–O3	110.96(6)
N–Na–O3	128.37(7)	O1–Na–O3a	78.61(6)

Table 7. Selected Bond Distances (Å) and Angles (deg) for **5**

	Bond Lengths		
Ba–N	3.045(4)	Ba–O3′	2.788(3)
Ba–O1	2.780(3)	Ba–O11	2.941(3)
Ba–O2	2.794(4)	Ba–O13a	2.989(3)
Ba–O3	2.752(4)	Cl1–O11	1.410(4)
Ba–N′	3.065(4)	Cl1–O12	1.403(5)
Ba–O1′	2.743(4)	Cl1–O13	1.410(4)
Ba–O2′	2.804(4)	Cl1–O14	1.456(4)
	Bond Angles		
N–Ba–O1	59.7(1)	C3–N–C5	110.2(4)
O1–Ba–O2	86.0(1)	Ba–O1–C2	117.9(3)
O1–Ba–O3	110.5(1)	Ba–O2–C4	126.7(3)
N–Ba–N′	156.6(1)	Ba–O3–C6	125.7(3)
N–Ba–O2	57.7(1)	Ba–O1′–C2′	128.7(2)
N–Ba–O3	57.7(1)	Ba–O2′–C4	127.2(3)
O2–Ba–O3	85.1(1)	Ba–O3′–C6′	116.4(2)
C1–N–C3	108.9(4)	O12–Cl1–O14	109.9(2)
C1–N–C5	111.6(4)	O11–Cl1–O13	111.3(2)

Results and Discussion

Syntheses of 1–5. Compound **1** was synthesized by combining a dilute aqueous solution of $HClO_4$ with TEA at 0 °C. In connection with another project,[14] crystals of this compound were formed accidentally in an attempt to recrystallize [$Me_3C{\equiv}NSi(OCH_2CH_2)_3N$]$ClO_4$. Because septa used to close the crystallizing tube are not impervious to moisture, adventitious water was responsible for the slow formation of a few crystals that turned out to be **1**:

$$[Me_3C{\equiv}NSi(OCH_2CH_2)_3N]ClO_4 + 4H_2O \rightarrow \mathbf{1} + Si(OH)_4 + Me_3CN \quad (1)$$

We have also synthesized **1** by the combination of equimolar aqueous solutions of $HClO_4$ and TEA, obtaining a 55% yield after purification. Using nonaqueous solvents, compounds **2** and **3** were made in a similar manner in 46 and 34% yields, respectively, and **4** and **5** were synthesized in 46 and 98% yields, respectively, using a 2:1 molar ratio of TEA to metal perchlorate.

Spectra. The ^1H and ^{13}C NMR spectral data for **1–5** are consistent with complexation of TEA to the cation although the shifts are generally not dramatic (0 to 0.3 ppm downfield in the case of ^1H and 0 to 4 ppm upfield for ^{13}C NMR spectra). The exception is the 0.9 ppm downfield shift for the NCH_2 protons of **1** relative to free TEA, which reflects the placement of a full

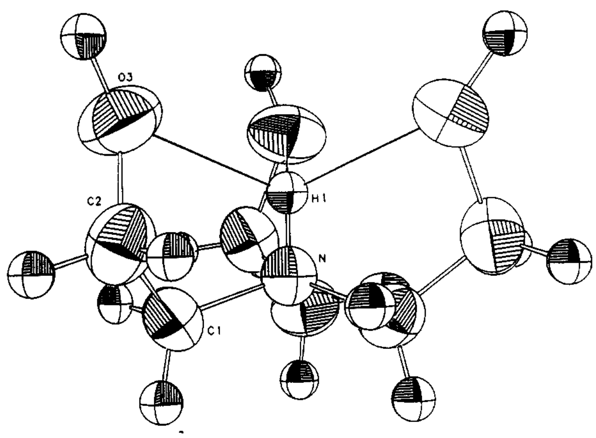


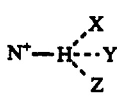
Figure 1. ORTEP drawing of 1. The ellipsoids are drawn at the 50% probability level.

positive charge on the tertiary nitrogen in this ammonium salt. The fact that no peak for the NH proton of this compound was observed suggests that exchange with the OH protons occurs.

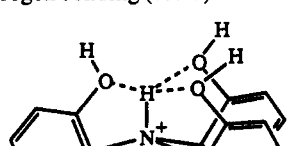
The ^1H NMR spectrum of **2** also revealed the presence of 0.4 THF per molecule of **2**. Upon addition of variable amounts of TEA to the NMR sample tube, only one pair of triplets was observed, attesting to the labile nature of this complex as well. This conclusion is further supported by the strong dependency of the ^7Li NMR shift on solvent (CD_3CN, δ –1.05; CD_3OD, δ –0.35). The remarkably narrow line width (80 Hz) of the ^7Li ($I = {}^3/_2$) MAS peak at δ 0.1 is consonant with a symmetrical environment (probably C_3) around the lithium. The substantially broader ^{23}Na ($I = {}^3/_2$) MAS peak for **3** (δ –14, $\Delta\nu_{1/2}$ = 850 Hz) suggests a less symmetrical environment for this nucleus, which is borne out by X-ray studies (see later).

Compounds **2** and **3** give intense peaks for the corresponding $M(TEA)^+$ cations in their FAB mass spectra while **5** exhibits a strong $Ba(TEA)_2ClO_4^+$ peak. The IR spectra in KBr pellets indicate the presence of both free (~3600 cm^{-1} [18]) and hydrogen-bound (~3300 cm^{-1} [18]) OH groups. Although the 1000–1300-cm^{-1} region can be informative regarding the coordination of the ClO_4^- ion,[19,20] this region is obscured by C–N and C–O bands from the TEA ligand.

Structural Features. The cation of **1** (Figure 1) contains a rare example of trifurcated hydrogen bonding (see **C**) shown to possess



C



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3-fold symmetry (i.e., X = Y = Z).[21,22] The hydrogen-bonding distance of the NH proton (which was located) to the alcoholic oxygens is 2.242(2) Å, while this distance from the OH protons (which were also located) to generally positioned ClO_4^- oxygens is 1.943(3) Å. A second oxygen of the ClO_4^- ion is hydrogen-bonded to a neighboring cation, resulting in a polymeric structure consisting of parallel sheets (Figure 2). The N–H distance of 0.92(6) Å in **1** is in good agreement with previous values of

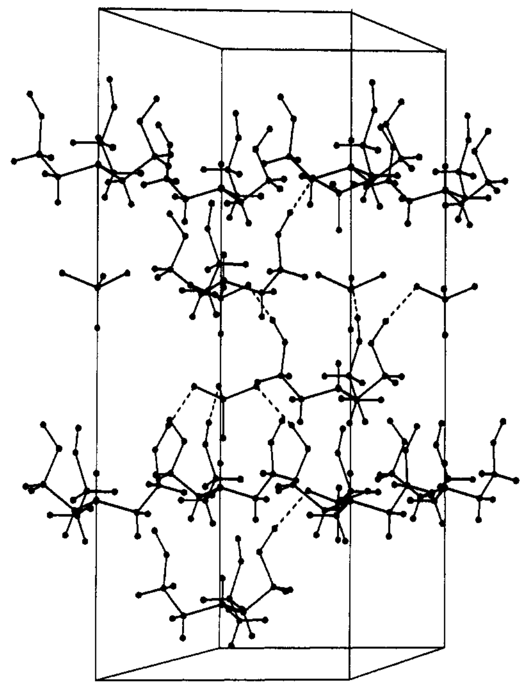

Figure 2. Molecular structure of 1.

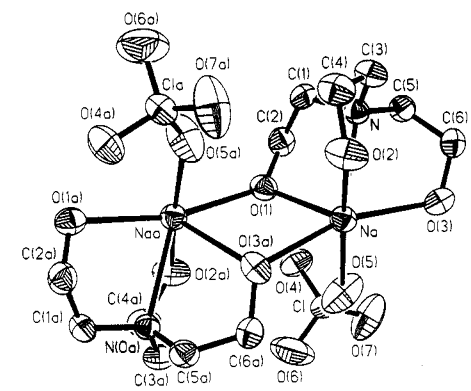

Figure 3. ORTEP drawing of 3. The ellipsoids are drawn at the 50% probability level.

0.92,[23] 1.01(6),[24] 0.84(5),[25] and 0.91(6) Å[26] reported for $H(TEA)O_2CCH_2OPh$, $H(TEA)O_2CCH_2SC_6H_4$-*p*-Cl, $H(TEA)NO_3$, and **6**(O_3SPh), respectively. In the first and last compounds all the protons were located, but this was not the case for the OH protons in the second. In all three cases extensive hydrogen bonding via the anion was reported.

The seven-coordinated sodium ion in **3** is bonded to the four heteroatoms of a TEA molecule, an oxygen of a perchlorate (Figure 3), and the oxygen of an OH group from each of two neighboring cations. The structure of **3** differs in this respect from that of Na(TEA)I,[11] wherein two OH groups from each molecule bridge two seven-coordinate Na^+ ions. In **3** the bridging OH groups form chains wherein extensive hydrogen bonding with ClO_4^- groups gives rise to a parallel sheet structure (Figure 4). In Na(TEA)I, the bridging leads to chain formation parallel to (100).[11] The average Na–OH distance in **3** is 2.500(2) Å, which is only somewhat shorter than the Na–N distance of 2.611(2) Å. This small difference could arise from the necessity for some of

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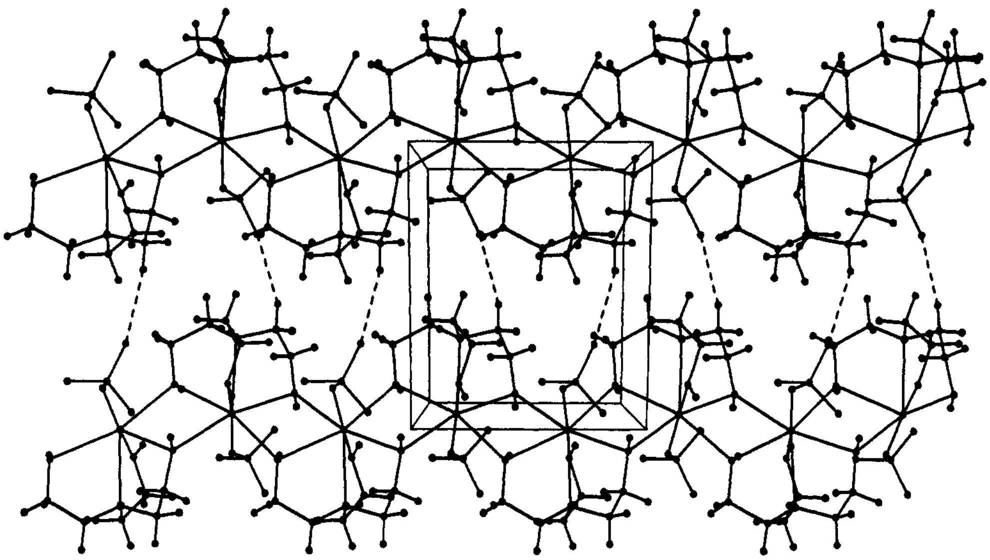

Figure 4. Molecular structure of 3. To more clearly illustrate interlayer hydrogen bonding, only one of the two chains in each layer traversing the unit cell is shown.

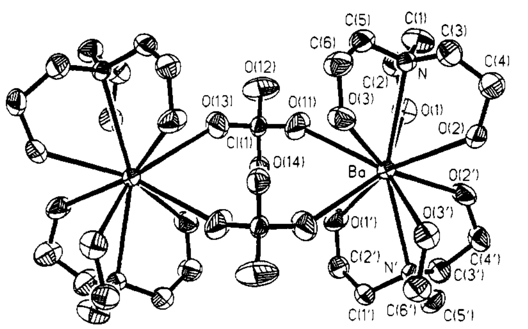

Figure 5. ORTEP drawing of 5. The ellipsoids are drawn at the 50% probability level.

the OH groups to share some of their electron density through bridging, thus lengthening the Na–OH distance. A similar small difference is observed in Na(TEA)I, in which there is also OH bridging.

That the perchlorate coordination to Na^+ in 3 is weak is shown by the similarity of the Cl–O5 length (1.412(2) Å) to the average of the other Cl–O distances (average 1.416(2) Å). A similar structural result has also been reported for perchlorates of a copper(II)[19] and a cobalt(III)[27] complex. In strongly coordinated perchlorate complexes, this difference is typically ca. 0.08 Å,[28] while in weakly coordinated complexes it would be 0–0.02 Å.[19,27]

From the ORTEP drawing of 5 in Figure 5 it is seen that both Ba^{2+} ions in the dimeric structure are ten-coordinate with two perchlorates acting as bridging groups. The average Ba–OH distance (2.776(4) Å) and the average Ba–N distance (3.056(4) Å) compare favorably with the corresponding values reported for other barium derivatives of TEA.[4–8] As in 3, coordination of the perchlorates in 5 is apparently weak according to the near-equality of the Cl–OBa and Cl–O distances. In Figure 6 is shown the extensive hydrogen bonding which pervades this structure. An oxygen of the non-barium-bridging perchlorate hydrogen-bridges OH groups on separate dimers, while two other oxygens hydrogen-bridge two other OH groups on separate dimers via a OH---OClO---HO linkage. This hydrogen-bonding scheme gives rise to infinite chains of dimers. The remaining oxygen on the perchlorate cross-links the chains into sheets separated only by van der Waals contacts.

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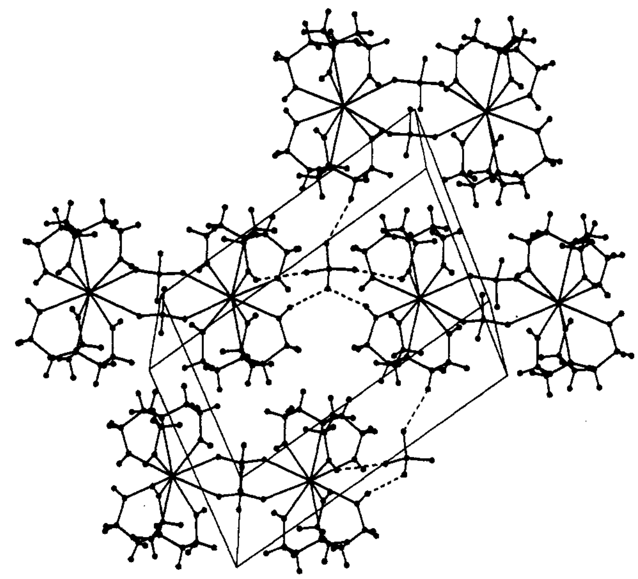

Figure 6. Molecular structure of 5.

Conclusions. Whereas TEA satisfies its hydrogen-bonding tendency internally in the solid state by forming discrete cagelike dimers, the introduction of a positive ion can separate the TEA moieties of the cage partially (as in the case of $[Ba(TEA)_2ClO_4]_2(ClO_4)_2$ (**5**)) or completely (e.g., $H(TEA)ClO_4$ (**1**)) causing the OH protons to seek oxygens on ClO_4^- anions with which they can hydrogen-bond, forming parallel sheet structures. In the case of the Na^+ complex 3, the structure is complicated by metal bridging by OH oxygens. Except in the case of 1, the ClO_4^- ion is a noninnocent ligand, coordinating as a monodentate ligand to the Na^+ in 3 and bridging two Ba^{2+} ions in 5 in a bidentate fashion. The perchlorate coordination in both cases is apparently weak, however.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research in the form of a grant to J.G.V. and to the Deutsche Forschungs Gemeinschaft for a postdoctoral fellowship to W.P.

Supplementary Material Available: Tables of crystal data, bond distances, bond angles, hydrogen atom positional parameters, and general displacement parameter expressions (24 pages). Ordering information is given on any current masthead page.