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Alkali and alkaline earth metal chloride complexes of triethanolamine: the structure of $[Sr(TEA)_2]Cl_2$

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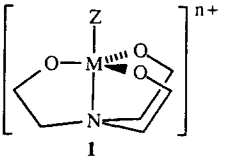
Abstract—The title triethanolamine (TEA) complexes isolated include M(TEA)Cl where M = Li (**1**), Na (**2**), K (**3**), Rb (**4**), Cs (**5**) and $M(TEA)_2Cl_2$ where M = Mg (**6**), Ca (**7**), Sr (**8**), Ba (**9**). These compounds were characterized by ^1H NMR, ^{13}C NMR and mass (FAB) spectroscopies, by elemental analysis and where appropriate by ^7Li and ^{23}Na NMR spectroscopies. In our hands the constitutions of **7** and **8** differ from those reported by others. The molecular structure of **8**, determined by X-ray means, reveals strontium ions bound to two tetradentate TEA molecules. Substantial hydrogen bonding to chlorides in the structure is also evident. Four out of the 20 molecules in the unit cell are also coordinated to a water molecule. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: triethanolamine; alkaline earth; alkaline metal; complexes.

In spite of the fact that triethanolamine (TEA), a tetracoordinating ligand, has been extensively used to prepare alkoxides of type **1** where M = Ti [1], Bi [2], V [3], B [4], Al [5], Fe [6], a group 14 element [7] or a group 15 element [8], its ability as a coordinating ligand to synthesize compounds of type **2** has not been extensively investigated. Prior to the initiation of this work, there were only two reports for complexes of type **2a** [9], namely a sodium iodide complex reported by others [9a] as well as lithium and sodium perchlorate complexes described by us [9b]. Several examples of type **2b** complexes have been reported wherein M = Sr and Ba [9b,10–16]. Because the perchlorate ion in $Na(TEA)ClO_4$ and $Ba(TEA)_2(ClO_4)_2$ were found by X-ray crystallography to be coordinated to the metal we decided to attempt the synthesis and characterization of TEA complexes of Groups I and II metal chlorides in order to determine if chloride tends to coordinate to the metal in the solid state. Herein we report the preparation of M(TEA)Cl, where M = Li (**1**), Na (**2**), K (**3**), Rb (**4**) and Cs (**5**) and $M(TEA)_2Cl_2$ where M = Mg (**6**), Ca (**7**), Sr (**8**) and Ba (**9**). These compounds were characterized by ^1H NMR, ^{13}C NMR and mass (FAB) spectroscopies and by elemental analysis, and where appropriate by ^7Li and ^{23}Na NMR spectroscopies. The molecular structure of **8** was determined by X-ray crystallography.



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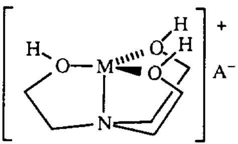
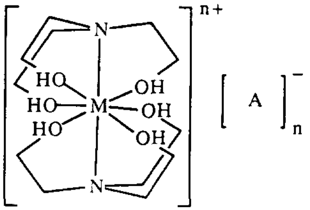


2a



2b

The reaction of TEA with $CaCl_2$ [14–15] and $SrCl_2$ [16] has been described by others. However, in the present work it is shown that the products of these reactions are different from those described earlier.

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EXPERIMENTAL

^{1}H, ^{13}C, ^{7}Li and ^{23}Na 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. X-ray diffraction experiments on powders were carried out on a Scintag XDS-2000 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Starting materials were purchased from Aldrich Chemical Company and were used without further purification. All melting points were measured using a Thomas Hoover capillary apparatus and are uncorrected.

Preparation of Li(TEA)Cl (**1**)

LiCl (3.32 g, 78.2 mmol) was dissolved in 50 cm^3 of distilled water. To this solution was added dropwise at room temperature 10.4 cm^3 (11.7 g, 78.2 mmol) of TEA. After the reaction mixture had been stirred for 20 h, the majority of the water was removed with a rotary evaporator. To the remaining solution was added about 30 cm^3 of acetone and 50 cm^3 of ether to produce a white precipitate which was separated by filtration and washed with 100 cm^3 of ether and dried *in vacuo*. Yield 74.6%. m.p. 139–140°C (dec). ^{1}H NMR (CD_3OD) δ 4.78 (s, 3 H, OH), 3.47 (t, 6 H, OCH_2, $^3J_{HH} = 5.4$ Hz), 2.52 (t, 6 H, NCH_2, $^3J_{HH} = 5.4$ Hz). ^{13}C NMR (CD_3OD) δ 60.13 (OCH_2) 57.05 (NCH_2). ^{7}Li NMR (D_2O) δ −0.12. MS, *m/z* 191 (M^+), 156 (M^+—Cl), 150 (TEA + H)$^+$, 118 (TEA —CH_2OH). Found: C, 37.5; H, 6.3. Calc. for $C_6H_{15}ClLiNO_3$: C, 37.6; H, 6.7%.

Preparation of Na(TEA)Cl (**2**)

The procedure was the same as for **1** except that NaCl was used instead of LiCl. Yield: 60.8%. m.p. 151–153°C (dec). ^{1}H NMR (D_2O) δ 4.67 (s, 3H, OH), 3.66 (t, 6 H, OCH_2, $^3J_{HH} = 5.4$ Hz), 2.71 (t, 6 H, NCH_2, $^3J_{HH} = 5.4$ Hz). ^{13}C NMR (D_2O, CH_3OH as external reference) δ 58.88 (OCH_2), 55.67 (NCH_2). ^{23}Na NMR (D_2O) δ −0.43. MS, *m/z* 207 (M^+), 150 (TEA + H^+), 149 (TEA).

Preparation of K(TEA)Cl (**3**)

The procedure is the same as that for **1** except that KCl was used. The final product was crystallized by cooling a hot concentrated water solution to room temperature. Yield: 30.05%. m.p. 223–226°C (dec). ^{1}H (D_2O) δ 4.67 (s, 3H, OH), 3.68 (t, 6 H, OCH_2, $^3J_{HH} = 6.2$ Hz), 2.72 (t, 6 H, OCH_2, $^3J_{HH} = 6.2$ Hz). ^{13}C NMR (D_2O, MeOH external reference) δ 58.78 (OCH_2), 55.67 (NCH_2). MS, *m/z* 223 (M^+), 188 (M^+—Cl), 150 (TEA + H^+). Found: C, 32.4; H, 6.7. Calc. for $C_6H_{15}ClKNO_3$: C, 32.2; H, 6.8%.

Preparation of Rb(TEA)Cl (**4**)

The procedure is the same as that for **3** except that RbCl was used. Yield: 24.5%. m.p. 201–202°C (dec). ^{1}H NMR (D_2O) δ 4.67 (s, 3 H, OH), 3.63 (t, 6 H, OCH_2, $^3J_{HH} = 5.1$ Hz), 2.68 (t, 6 H, NCH_2, $^3J_{HH} = 5.1$ Hz). MS *m/z* 269 (M^+), 150 (TEA + H^+). Found: C, 27.2; H, 5.7. Calc. for $C_6H_{15}ClNO_3Rb$: C, 26.8; H, 5.6%.

Preparation of Cs(TEA)Cl (**5**)

The procedure is the same as that for **1** except that CsCl was used instead of LiCl. Yield 24.7%. m.p. 123–125°C (dec). ^{1}H NMR (D_2O) δ 4.67 (s, 3 H, OH), 3.73 (t, 6 H, OCH_2, $^3J_{HH} = 5.2$ Hz), 2.79 (t, 6 H, NCH_2, $^3J_{HH} = 5.2$ Hz). ^{13}C NMR (D_2O) δ 58.82 (OCH_2), 55.69 (NCH_2). MS *m/z* 317 (M^+), 150 (TEA + H^+), 133 (Cs^+).

Preparation of $Mg(TEA)_2Cl_2 \cdot H_2O$ (**6**)

To a solution of 1.24 g (13.0 mmol) of $MgCl_2$ in 100 cm^3 of H_2O was added 3.50 ml (3.92 g, 26.3 mmol) of TEA. After the reaction flask was stirred for 20 h at room temperature, the solvent was removed by rotary evaporator and the solid was washed with 200 cm^3 of ether and then dried *in vacuo*. Yield = 87.8%. m.p. 161–162°C (dec). ^{1}H NMR (D_2O) δ 4.67 (s, 6 H, OH), 3.59 (t, 12 H, OCH_2, $^3J_{HH} = 5.1$ Hz), 2.65 (t, 12 H, NCH_2, $^3J_{HH} = 5.1$ Hz). ^{13}C NMR (D_2O, CH_3OH as external standard) δ 58.89 (OCH_2), 55.75 (NCH_2). ^{13}C MAS NMR (25.18 Hz) δ 59.33 (OCH_2), 55.81 (NCH_2), MS *m/z* 412 ($M + H^+$), 394 ($M + H^+$—H_2O), 358 (M^+—Cl—H_2O). Found: C, 34.7; H, 8.1. Calc. for $C_{12}H_{32}Cl_2MgN_2O_7$: C, 35.0; H, 7.8%.

Preparation of $Ca(TEA)_2Cl_2 \cdot 5H_2O$ (**7**)

The procedure is the same as that for **6** except that $CaCl_2$ was used instead of $MgCl_2$ and the final product was crystallized by cooling a hot concentrated aqueous solution of **7** to room temperature. Yield 85%. m.p. 62°C (with decomposition). ^{1}H NMR (CD_3OD) δ 4.89 (s, 16 H, OH and H_2O), 3.76 (t, 12 H, OCH_2, $^3J_{HH} = 5.3$ Hz), 2.88 (t, 12 H, NCH_2, $^3J_{HH} = 5.3$ Hz). ^{1}H NMR (D_2O) δ 4.67 (s, 16 H, OH and H_2O), 3.57 (t, 12 H, OCH_2, $^3J_{HH} = 5.3$ Hz), 2.58 (t, 12 H, NCH_2, $^3J_{HH} = 5.3$ Hz). ^{13}C NMR (CD_3OD) δ 59.22 (OCH_2), 55.87 (NCH_2). MS *m/z* 409 (M^+—Cl—$3H_2O$), 391 (M^+—Cl—$4H_2O$), 373 (M^+—Cl—$5H_2O$), 224 (M^+—Cl—$5H_2O$—TEA), 150 (TEA + H^+), 149 (TEA^+).

Preparation of $Sr(TEA)_2Cl_2$ (**8**)

To a solution of 2.66 g (10.0 mmol) of $SrCl_2 \cdot 6H_2O$ in 100 cm^3 of MeOH was added 2.65 cm^3 (2.97 g, 19.9

mmol) of TEA. After stirring for 12 h, the majority of the solvent was removed *in vacuo* and to the remaining solution was slowly added 50 cm^3 of ether. After storing at room temperature for 6 h, small crystals of product appeared. Yield 80%. m.p. 115–116°C. ^1H NMR (CD_3OD) δ 4.89 (s, 6 H, OH), 3.76 (t, 12 H, OCH_2, $^3J_{HH} = 5.7$ Hz), 2.68 (t, 12 H, NCH_2). ^{13}C NMR (CD_3OD) δ 59.70 (OCH_2), 56.84 (NCH_2). MS-FAB *m/z* 421 (M^+—Cl), 272 (M^+—Cl—TEA), 150 (TEA + H^+). Found: C, 30.4; H, 6.5. Calc. for $C_{12}H_{30}Cl_2N_2O_6Sr$: C, 31.5; H, 6.6%. An X-ray quality crystal was obtained by slow diffusion of a layer of ether into a methanol solution of **8** over a period of 3 days.

Preparation of $Ba(TEA)_2Cl_2$ (9)

To a suspension of $BaCl_2 \cdot 2H_2O$ (2.73 g, 11.2 mmol) in 100 cm^3 of water was added 2.97 cm^3 (3.32 g, 22.2 mmol) of TEA at room temperature. After refluxing for 20 h, all the solvent was removed with a rotary evaporator. The remaining solid was washed with 100 cm^3 of ether and dried *in vacuo*. Yield 89.7%. m.p. 120°C (dec). ^1H NMR (D_2O) δ 4.67 (s, 6 H, OH), 3.57 (t, 12 H, OCH_2, $^3J_{HH} = 6$ Hz), 2.69 (t, 12 H, NCH_2, $^3J_{HH} = 6$ Hz). ^{13}C NMR (D_2O, MeOH as external standard) δ 58.92 (OCH_2), 55.75 (NCH_2). MS, *m/z* 471 (M^+—Cl), 322 (M^+—Cl—TEA).

X-ray analysis of 8

A crystal of **8** was mounted on a glass fiber on the Siemens P4RA for data collection at 213 ± 1 K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. Twenty-five reflections in the range 11.78–16.38° θ were used to determine precise cell constants. Lorentz and polarization corrections were applied. A nonlinear correction based on the decay in the standard reflections was also applied to the data. A series of azimuthal reflections was collected for this specimen and a semi-empirical absorption correction was applied to the data [17]. The space group *C2/c* was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as determined by a successful direct-methods solution [17] and subsequent refinement. Most non-hydrogen atoms were placed directly from the E-map. The remaining missing atoms were placed in the course of several least squares/difference-Fourier cycles. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as riding-atoms with individual isotropic displacement parameters. The hydroxyl hydrogens were refined with a group isotropic displacement parameter. Final refinements were done with SHELXL-93 [18,19]. The data collection and structure solution were conducted at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment MicroVAX 3100 computer using SHELXTL-Plus [17] and on a DECStation 5000 computer using SHELXL-93 [18]. Pertinent data collection and refinement data are collected in Table 1 and selected bond lengths and distances appear in Table 2.

RESULTS AND DISCUSSION

Addition of an equimolar amount of TEA to a Group IA metal chloride resulted in the formation of M(TEA)Cl according to reaction (1)

$$\mathrm{MCl + TEA \longrightarrow M(TEA)Cl}$$
$$\mathrm{M = Li\,(\mathbf{1}), Na\,(\mathbf{2}), K\,(\mathbf{3}), Rb\,(\mathbf{4}), Cs\,(\mathbf{5})} \quad (1)$$

while the reaction of two moles of TEA with a Group IIA metal chloride gave $M(TEA)_2Cl_2$ according to reaction (2).

$$\mathrm{MCl_2 + 2TEA \longrightarrow M(TEA)_2Cl_2}$$
$$\mathrm{M = Mg\cdot H_2O\,(\mathbf{6}) \quad Sr\,(\mathbf{8})} \quad (2)$$
$$\mathrm{Ca\cdot 5H_2O\,(\mathbf{7}) \quad Ba\,(\mathbf{9})}$$

As expected, the ^1H and ^{13}C NMR spectra for these compounds are simple. In the ^1H NMR spectra a singlet for three OH groups of TEA and two triplets for two methylene groups were consistently observed. The ^1H NMR spectrum of **7** also shows the presence of *ca.* five molecules of water. Our isolation of this compound is in contrast with an earlier report that no reaction occurred when two moles of TEA were added to one mole of $CaCl_2$ [15], and a second report that anhydrous $Ca(TEA)Cl_2$ was formed in the same reaction [14]. Our mass spectroscopic experiments also showed the presence of water in **7**.

Among the reported complexes of TEA, only three compounds have been shown by X-ray crystallography to have solvent in their molecular structures, namely, $Ln(TEA)_2(CF_3SO_3)_3(THF)_3$ where Ln = Pr and Yb [20] and $Y(TEA)_2(ClO_4)_3(py)_3$ [21]. In the first two compounds, one THF molecule coordinates to the lanthanide, the second is hydrogen bonded to the OH groups of TEA while the third THF is present only as a solvent of crystallization [20]. In $Y(TEA)_2(ClO_4)_3(py)_3$, however, all three pyridine molecules are hydrogen bonded to the three OH groups of one TEA [21]. Although it has been reported that $SrCl_2 \cdot 6H_2O$ and TEA react to produce the trihydrate $Sr(TEA)_2Cl_2(H_2O)_3$ [16], the ^1H NMR, MS and elemental analysis of the compound obtained in the present work indicate that a much less hydrated form of $Sr(TEA)_2Cl_2$ has been synthesized. Crystals suitable for X-ray study were grown *via* slow diffusion of a layer of ether into a solution of **8** in methanol. A thermal ellipsoid drawing of the cation of **8** in the three forms it occurs in the crystal structure is shown in Fig. 1(a)–(c). The molecular structure of **8** features 20 molecules per unit cell, four of which are hydrated with one water molecule coordinated to the metal. It

Table 1. Crystallographic data for **8**

Formula	$C_{12}H_{30.4}Cl_2N_2O_{6.20}Sr$
M	460.50
Space group	$C2/c$
a (Å)	51.515(5)
b (Å)	7.3101(7)
c (Å)	29.441(3)
α (°)	90.0
β (°)	117.960(8)
γ (°)	90.0
V (Å^3)	9792.7(19)
Z	20
μ(Cu-K_α)(mm^{-1})	6.599
F	4760
Data collection instrument	Siemens P4RA
Temp (K)	213(1)
R[a]	0.0481
	0.1226
R_w[b]	0.1266

[a] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.

[b] $R_w = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{0.5}$ where $w = 1/[\sigma^2(F_0^2) + (a^*P)^2 + b^*P + d + e^*\sin\theta]$.

Table 2. Selected bond distances (Å) and angles (°) for **8**

Sr—N(1)	2.753(4)	Sr′—O(1′) # 1[a]	2.627(3)
Sr—N(2)	2.766(4)	Sr′—N(1′) # 1[a]	2.800(4)
Sr′—O(3′) # 1[a]	2.595(3)	Sr′—N(1′)	2.800(4)
Sr′—O′	2.604(5)	Sr″—N(2″)	2.787(4)
Sr′—O(2′) # 1[a]	2.610(3)	Sr″—N(1″)	2.845(4)
N(1)—Sr—N(2)	152.77(11)	O(2′) # 1—Sr′—N(1′) # 1	64.74(10)
O(3′) # 1—Sr′—O′	76.11(9)	O(1′) # 1—Sr′—N(1′) # 1	64.01(10)
O(3′) # 1—Sr′—O(2′) # 1	96.98(11)	O(3′) # 1—Sr′—N(1′)	127.06(10)
O′—Sr′—O(2′) # 1	65.75(7)	O′—Sr′—N(1′)	109.25(7)
O(3′) # 1—Sr′—O(1′) # 1	123.25(11)	O(2′) # 1—Sr′—N(1′)	134.23(10)
O′—Sr′—O(1′) # 1	142.53(8)	O(1′) # 1—Sr′—N(1′)	85.11(10)
O(2′) # 1—Sr′—O(1′) # 1	79.33(11)	N(1′) # 1—Sr′—N(1′)	141.5(2)
O(3′) # 1—Sr′—N(1′) # 1	63.62(10)	N(2″)—Sr″—N(1″)	166.29(11)
O′—Sr′—N(1′) # 1	109.25(8)		

[a] The symmetry transformations used to generate equivalent atoms were $-x, y, -z + 1/2$.

is surmised that adventitious water was responsible for this partial hydration. All the chlorides in the unit cell are hydrogen bound to OH groups of the TEA, forming hydrogen bonds in the range 2.2–2.36 Å. None of the chlorides coordinate to the metal in contrast to perchlorate in the case of Ba(TEA)(ClO_4)$_2$ [9b]. The only other hydrogen bond appears to be an intramolecular one involving a water hydrogen and a TEA oxygen: O′—H′···O(1′) = 2.484 Å. As expected, the N—Sr—N angle is most acute for the hydrated molecules of **8** (141.5°) while these angles for the other molecules are less acute [N(1)—Sr—N(2) = 152.75° and N(1″)—Sr″—N(2″) = 166.28°].

The average Sr—O(TEA) distances in the hydrated and anhydrous molecules are 2.610(3) and 2.550(4) Å, respectively. These distances closely match those reported for Sr(TEA)$_2$(NO_3)$_2$ (2.560(4) Å) [11] and Sr(TEA)$_2$(N_3)$_2$ (2.544(6) Å) [10]. The Sr—N distances in the hydrated and unhydrated molecules of 2.800(4) and 2.787(4) Å, respectively, are also similar to those reported for Sr(TEA)$_2$(NO_3)$_2$ (2.830(4) Å) [11] and Sr(TEA)$_2$(N_3)$_2$ (2.798(18) Å) [10].

The MS data for compounds **1**–**5** show that only one TEA is coordinated to the metal regardless of the size of the nucleus. This is interesting because large ions such as Rb^+ or Cs^+ could be ligated by two molecules of TEA. The low charge on these large ions undoubtedly precludes this with TEA, however. It should be noted, that the metal atom of Na(TEA)I, characterized earlier by X-ray analysis, has a coordination number of seven [9]. Thus in addition to the

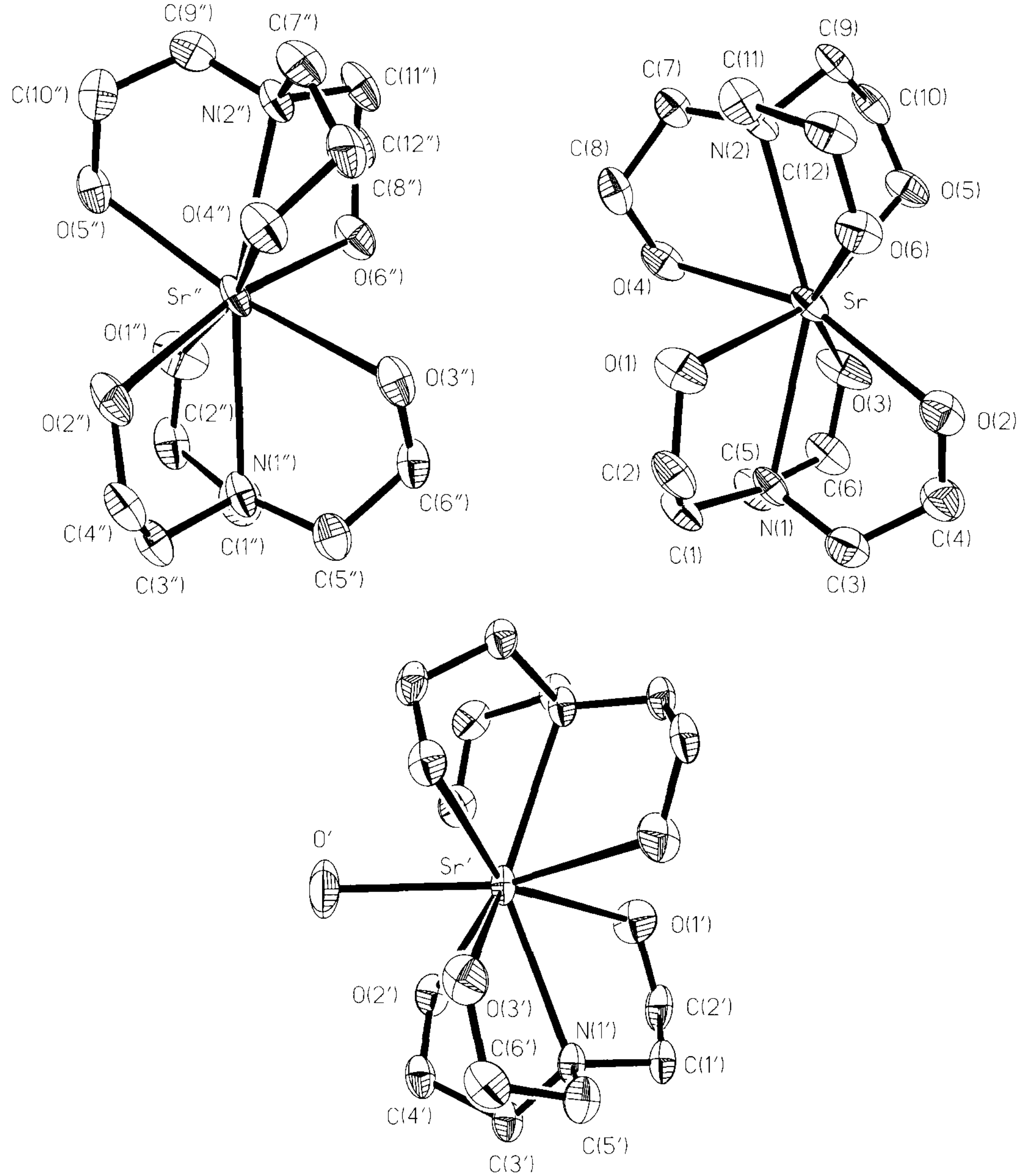

Fig. 1. Computer drawing of the three kinds of molecules of **8** found in the unit cell. Ellipsoids are drawn at the 50% probability level.

coordination of four atoms from TEA, the iodine and two oxygen atoms from neighboring molecules are also coordinated to the metal [9]. In **1** to **5** it is also possible that oxygen atoms of a neighboring coordinated TEA satisfy the high coordination numbers associated with some of the large metal ions in this series. It is noteworthy that the bond between the Cs atom and TEA is relatively weak and it is easily disrupted above 120°C at atmospheric pressure. Under reduced pressure at a temperature as low as 60°C, the breakage of the coordinate bonds was indicated by evaporation of the ligand. When compounds **7** and **8** were heated to 600°C, the only product detectable by X-ray powder diffraction was $CaCl_2$ and $SrCl_2$, respectively. No CaO or SrO was observed.

The ^{13}C NMR spectra of compounds **1**–**9** show only two peaks corresponding to the OCH_2 and NCH_2 carbons. ^{13}C NMR spectra run both in solution (D_2O) and in the solid state for **6** revealed very similar chemical shifts. ^{7}Li and ^{23}Na NMR chemical shifts for 4 M solutions of **1** and **2** in D_2O/H_2O were compared with a 4 M solution of the parent salts LiCl and NaCl, respectively. In both cases the chemical shifts were quite similar to those of the starting materials. Thus in water the TEA ligand is apparently labile to water substitution. That TEA is coordinated to the metal in

1–**9** in the solid state is supported by the mass spectral results given in the Experimental Section and confirmatory evidence of this conclusion is gained from the X-ray structure of **8**.

Supplementary material

Tables of anisotropic thermal parameters, hydrogen atom parameters, complete bond lengths and angles, torsion angles and observed and calculated structural factors can be obtained from the authors upon request.

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REFERENCES

1. (a) A. A. Naiini, S. L. Ringrose, Y. Su, R. A. Jacobson and J. G. Verkade, *Inorg. Chem.* 1993, **32,** 1290; (b) A. A. Naiini, W. M. P. B. Menge and J. G. Verkade, *Inorg. Chem.* 1991, **30,** 5009; (c) W. Menge and J. G. Verkade, *Inorg. Chem.* 1991, **30,** 4628; (d) R. Taube and P. Knoth, *Anorg. Allg. Chem.* 1990, **581,** 89; (e) R. L. Haclau, *Acta Cryst., C*39 1983, 1344. (f) H. J. Cohen, *J. Organomet. Chem.* 1967, **9,** 177; (g) M. G. Voronkov and F. D. Faitel'son, *Khim. Geterotsikl. Soedin.* 1967, 39; *Chem. Abstr.* 1967, **67,** 64321w.
2. W. T. Miller, *J. Am. Chem. Soc.* 1940, **62,** 2707.
3. (a) R. K. Mittal *Anorg. Allg. Chem.* 1967, **351,** 309; (b) E. E. Shestakov, M. G. Voronkov, Y. L. Frolov and V. P. Baryshok, *J. Gen. Chem. USSR* 1983, **53,** 1161.
4. E. Muller and H.-B. Burgi, *Helv. Chim. Acta* 1987, **70,** 499.
5. (a) J. Pinkas and J. G. Verkade, *Inorg. Chem.* 1993, **32,** 2711; (b) F. Hein and P. W. Albert, *Z. Anorg. Allg. Chem.* 1952, **269,** 67; (c) R. C. Mehrotra and R. K. Mehrotra, *Indian Chem. Soc.* 1962, **39,** 667; (d) M. J. Lacey and G. C. McDonald *Aust. J. Chem.* 1976, **29,** 1119; (e) M. G. Voronkov and V. P. Baryshok, *J. Organomet. Chem.* 1982, **239,** 199.
6. K. Stark, *J. Inorg. Nucl. Chem.* 1959, **11,** 77.
7. S. N. Tandura, M. G. Voronkov and N. V. Alekseev, *Top Curr. Chem.* 1986, **131,** 99.
8. (a) J. G. Verkade, *Acc. Chem. Res.* 1993, **26,** 483; (b) J. G. Verkade, *Coord. Chem. Rev., Main Group Chemistry Review* issue, 1994, **137,** 233.
9. (a) J. C. Voegele, J. Fischer and R. Weiss, *Acta Cryst., B*30 1974, 62; (b) A. A. Naiini, J. Pinkas, W. Plass, V. Young, Jr and J. G. Verkade, *Inorg. Chem.* 1994, **33,** 2137.
10. A. Taeb, H. Krishner and Ch. Kratky, *Z. Kristallogr.* 1986, **177,** 263.
11. J. C. Voegele, J. Fischer and R. Weiss, *Acta Cryst., B*30 1974, 66.
12. J. C. Voegele, J. L. Thierry and R. Weiss, *Acta Cryst., B*30 1974, 70.
13. J. A. Kanters, W. J. J. Smeets, K. Venkatasubramanian and N. S. Poonia, *Acta Cryst., C*40 1984, 1701.
14. J. A. Kanters, A. deKoster, A. Schouten, K. Venkatasubramanian and N. S. Poonia, *Acta Cryst., C*41 1985, 1585.
15. E. Jaffe, *Annall di Chimica Applicata* 1932, **22,** 737.
16. F. Gavelli, *IX Congr. Int. Qutm, Puraapl. Madred* 1934, **3,** 293.
17. SHELXTL-PLUS, G. M. Sheldrick, Siemens Analytical Xray, Inc., Madison, WI.
18. SHELXL-93, G. M. Sheldrick, in preparation.
19. All X-ray scattering factors and anomalous dispersion terms were obtained from the *International Tables for Crystallography*, Vol. C, pp. 4.2.6.8 and 6.1.1.4. Kynoch Press, Birmingham, U.K. (1974).
20. F. E. Hahn and J. Mohr, *Chem. Ber.* 1990, **123,** 481.
21. A. A. Naiini, V. Young and J. G. Verkade, *Polyhedron* 1995, **14,** 393.