NEW COMPLEXES OF TRIETHANOLAMINE (TEA): NOVEL STRUCTURAL FEATURES OF [Y(TEA)₂](ClO₄)₃·3C₅H₅N AND [Cd(TEA)₂](NO₃)₂

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Abstract—The synthesis and characterization of the triethanolamine (TEA) complexes $Sc(TEA)_2Cl_3$ (**1**), $Y(TEA)_2(ClO_4)_3 \cdot 3C_5H_5N$ (**2**), $Fe(TEA)_2Cl_3$ (**3**), $Ni(TEA)_2Cl_2$ (**4**), $Zn(TEA)_2Br_2$ (**5**), $Zn(TEA)_2(NO_3)_2$ (**6**), $Cd(TEA)_2Cl_2$ (**7**), $Cd(TEA)_2(NO_3)_2$ (**8**), $Pb(TEA)_2(OAc)_2$ (**9**) and $Bi(TEA)_2Cl_3$ (**10**) are reported. The structures of **2** and **8**, determined by X-ray diffraction, unexpectedly revealed eight-coordinate metals in both cases. Both structures adopt a distorted hexagonal bipyramidal configuration in which the atoms in the hexagonal plane alternately fall above and below the plane. In **2**, the three pyridines as well as the three perchlorates are involved only in hydrogen bonding to the OH groups of different TEA ligands, causing a novel distortion of the coordination sphere. Compound **8** represents an unusual example of the relatively rare coordination number eight for cadmium(II).

There is considerable interest in convenient syntheses of precursors for the formation of materials *via* sol–gel[1] or low-temperature MOCVD techniques.[2] Although conventional metal alkoxides of the type $M(OR)_x$ have been widely studied for these purposes, far less emphasis thus far has been placed on compounds of this type derived from polyfunctional alcohols.

Triethanol amine (TEA) possesses advantages that make it worthy of study. Because of its chelating ability, TEA generally forms robust monomeric tricyclic ("atrane") structures of type **A** that

A
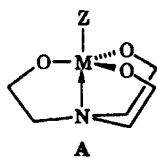
are easily solvolysable and in many cases are sublimable or distillable at relatively low temperatures.[3] Another advantage of TEA is that it is available commercially and is relatively inexpensive.

Although the first cationic complex of triethanolamine (TEA) was reported more than 60 years ago,[4] there have been few compounds of this class which have since then been described in the literature. Except for a recent paper describing the synthesis and characterization of $Ln[N(CH_2CH_2OH)_3]_2(CF_3SO_3)_3 \cdot (THF)_3$ (Ln = Pr, Yb and Lu),[5] complexes of TEA are limited to the alkali[6,7] and alkaline earth metal[7,8] derivatives. Here we examine the ability of TEA to stabilize main group metal ions (other than group 1 and 2) and also transition metal and lanthanide complexes, namely, $Sc(TEA)_2Cl_3$ (**1**), $Y(TEA)_2(ClO_4)_3 \cdot 3C_5H_5N$ (**2**), $Fe(TEA)_2Cl_3$ (**3**), $Ni(TEA)_2Cl_2$ (**4**), $Zn(TEA)_2Br_2$ (**5**), $Zn(TEA)_2(NO_3)_2$ (**6**), $Cd(TEA)_2Cl_2$ (**7**), $Cd(TEA)_2(NO_3)_2$ (**8**), $Pb(TEA)_2(OAc)_2$ (**9**) and $Bi(TEA)_2Cl_3$ (**10**). The crystal and molecular structures of the unexpectedly eight-coordinate metals in **2** and **8** are also described.

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EXPERIMENTAL

General procedure

^{1}H and ^{13}C NMR spectra were recorded on a Nicolet NT-300 or a Varian VXR-300 instrument. ^{113}Cd NMR spectra were recorded on a Bruker WM-200 and were referenced to a 0.1 M solution of Cd(NO$_3$)$_2$ at $\delta - 1.9$. ^{13}C solid state NMR spectra were measured with a Bruker MSL-300 instrument. FTIR spectra were recorded on an IBM-IR 98 spectrometer using Nujol mulls. FAB mass spectra were obtained on a Kratos MS 50 instrument. Melting points were determined with a Thomas Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by Desert Analytics, Tucson, Arizona. All starting materials were purchased from Aldrich Chemical Company and were used without further purification except triethanolamine which was distilled (145–155°C at 100 mTorr).

Preparation of Sc(TEA)$_2$Cl$_3$ (1)

To 2.0 g of ScCl$_3 \cdot x$H$_2$O dissolved in 100 cm^3 of acetone was added dropwise 2.5 cm^3 (2.8 g, 8.8 mmol) of triethanolamine at room temperature whereupon a copious precipitate formed. The reaction flask was stirred for 20 h and then the solid was filtered and washed with 200 cm^3 of ether and dried *in vacuo*, giving 3.5 g of product. Yield: 71%. Mp: 201–203°C. ^{1}H NMR (D$_2$O) δ 4.67 (s, 6 H, OH), 3.83 (t, 12 H, $^3J_{HH}$ = 5.1 Hz, OCH$_2$), 3.34 (t, 12 H, $^3J_{HH}$ = 5.1 Hz, NCH$_2$). ^{13}C (D$_2$O, MeOH used as external standard) 55.38 (CH$_2$O), 55.16 (CH$_2$N); MS (FAB), *m/z* 335 (M−Cl−H−TEA)$^+$, 299 (M−2Cl−TEA)$^+$, 150 (TEA+H)$^+$, 116 (ScCl$_2$)$^+$. IR (Nujol mull), 3320 (s,br), 3147 (sh), 2958 (s), 2855 (s), 1458 (s), 1402 (m), 1370 (m), 1303 (w), 1094 (w), 1030 (m), 916 (m), 888 (w), 722 (w), 608 (w), 528 (w).

Preparation of {Y[N(CH$_2$CH$_2$OH)$_3$]$_2$}(ClO$_4$)$_3 \cdot$ 3C$_5$H$_5$N (2)

Excess TEA (0.61 cm^3, 0.91 g, 6.1 mmol) was added to a stirred methanol solution of Y(ClO$_4$)$_3 \cdot$ 6 H$_2$O (1.0 g, 2.0 mmol) at room temperature. After the mixture was stirred for 15 h at room temperature, the solvent was removed on a rotatory evaporator giving a colorless oil. To this oil dissolved in 30 cm^3 of pyridine was added ether to precipitate a white solid. The solid was filtered and washed thoroughly with ether and then pentane, giving 1.3 g of final product. Yield: 72%. Crystals of X-ray quality were obtained overnight after careful lay-ering of a pyridine solution of 2 with ether. Mp: 145–147°C dec. ^{1}H NMR (D$_2$O): δ 8.35 (d, 6 H, $^3J_{HH}$ = 4.5 Hz, Py), 7.72 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, Py), 7.29 (m, 6 H, Py), 4.61 (s, 6 H, OH), 3.75 (t, 12 H, $^3J_{HH}$ = 5.4 Hz, OCH$_2$), 3.16 (t, 12 H, $^3J_{HH}$ = 5.4 Hz, NCH$_2$). ^{13}C NMR (D$_2$O, MeOH as external standard) δ 148.56, 137.926, 124.63 (Py), 55.65 (NCH$_2$), 55.48 (OCH$_2$). MS (FAB) was not successful. IR (Nujol mull): 3310 (sh), 3163 (s,br), 2953 (s), 2851 (s), 1597 (sh), 1445 (m), 1375 (w), 1249 (w), 1214 (w), 1159 (w), 1121 (m), 1006 (m), 1923 (m), 900 (m), 763 (m), 708 (m), 622 (m). Found: C, 35.0; H, 4.8. Calc for C$_{27}$H$_{45}$Cl$_3$N$_5$O$_{18}$Y: C, 35.1; H, 4.9%.

Preparation of Fe(TEA)$_2$Cl$_3$ (3)

To 3.63 g (13.4 mmol) of FeCl$_3 \cdot$ 6 H$_2$O dissolved in 100 cm^3 of distilled water was added dropwise at room temperature 3.57 cm^3 (4.00 g, 26.8 mmol) of TEA. The color of the reaction mixture changed from orange to deep red upon completion of the addition. After stirring for an additional 20 h, water was removed under vacuum and the solid was triturated first with 50 cm^3 of ether and then with the 50 cm^3 of THF before being dried *in vacuo* to provide 5.82 g of product. Yield: 85.4%. Mp: 99–110 (dec). ^{13}C NMR (D$_2$O, MeOH was used as external reference) δ 54.63 (OCH$_2$), 54.60 (NCH$_2$). MS (FAB), *m/z* 461 (M+H)$^+$, 390 (M−2Cl)$^+$, 241 (M−2Cl−TEA)$^+$, 213 ((M−Cl)/2)$^+$, 150 (TEA+H)$^+$. IR (Nujol mull) 3305 (br), 3130 (sh), 2952 (s), 2845 (s), 1461 (s), 1375 (m), 1340 (w), 1257 (w), 1092 (w), 1003 (m), 915 (w), 847 (w), 721 (m), 656 (w). Found: C, 30.7; H, 6.7. Calc for C$_{12}$H$_{30}$Cl$_3$FeN$_2$O$_6$: C, 31.2; H, 6.6%.

Preparation of Ni(TEA)$_2$Cl$_2$ (4)

The procedure for the preparation of **4** is the same as that for **3** except that 4.75 g (20.0 mmol) of NiCl$_2$ and 5.40 cm^3 (6.05 g, 40.6 mmol) of triethanol amine was used. Yield: 99.2%. The compound changed from blue to green at 179–181°C, decomposing at 225–227°C. ^{1}H NMR (D$_2$O) δ 4.67 (br, 6 H, OH), 3.47 (br, 12 H, OCH$_2$), 2.78 (br, 12 H, NCH$_2$). ^{13}C NMR (D$_2$O, MeOH used as external reference) 56.60 (OCH$_2$), 55.18 (NCH$_2$). MS (FAB), *m/z* 429 (M+H)$^+$, 392 (M−Cl)$^+$, 243 (M−Cl−TEA)$^+$, 150 (TEA+H)$^+$. IR (Nujol mull) 3508 (w), 3158 (s, br), 2945 (s), 2849 (s), 1454 (m), 1376 (w), 1329 (w), 1265 (w), 1223 (w), 1141 (w), 1079 (w), 1052 (m), 1005 (w), 822 (w), 752 (w), 722 (w), 667 (w). Found: C, 33.3; H, 7.0. Calc for C$_{12}$H$_{30}$Cl$_2$N$_2$NiO$_6$: C, 33.7; H, 7.1%.

Preparation of Zn(TEA)₂Br₂ (5)

The procedure for the preparation of **5** is the same as that for **1** except the reaction was done in ether. The product was insoluble in a variety of solvents, precluding solution NMR spectral analysis. Yield: 81.5%. Mp: 175–180°C (dec). ^{13}C NMR (CPMAS, spinning rate 2.7 kHz), 55.98 (OCH₂), 55.27 (NCH₂). MS (FAB), m/z 524 (M+H)⁺, 443 (M−Br)⁺, 294 (M−Br−TEA)⁺, 150 (TEA+H)⁺, 145 (NiBr)⁺. IR (Nujol mull) 3350 (br), 3150 (sh), 2922 (s), 2856 (s), 1485 (w), 1458 (m), 1406 (w), 1292 (w), 1250 (w), 1094 (w), 1072 (m), 1032 (m), 916 (m), 897 (w), 613 (m).

Preparation of Zn(TEA)₂(NO₃)₂ (6)

The procedure for the preparation of **6** is the same as that for **3** except that Zn(NO₃)₂·6H₂O (6.0 g, 20 mmol) was used and the reaction solvent was MeOH (40 mL). Yield: 80.2%. Mp: 103–105°C dec. ^{1}H NMR (D₂O) 4.67 (s, 6 H, OH), 3.70 (t, 12 H, $^{3}J_{HH}$ = 5.4 Hz, OCH₂), 3.08 (t, 12 H, $^{3}J_{HH}$ = 5.4 Hz, NCH₂). ^{13}C (D₂O, MeOH as external reference) 56.23 (OCH₂), 55.36 (NCH₂). MS (FAB), m/z 489 (M+H)⁺, 426 (M−NO₃)⁺, 277 (M−NO₃−TEA)⁺, 150 (TEA+H)⁺. IR (Nujol mull) 3352 (m, br), 3149 (sh), 2957 (s), 2849 (s), 1457 (s), 1376 (m), 1256 (w), 1216 (w), 1144 (w), 1092 (w), 984 (w), 823 (w), 722 (w), 633 (w), 525 (w).

Preparation of Cd(TEA)₂Cl₂ (7)

To 4.4 g (19 mmol) of CdCl₂·2.5 H₂O dissolved in 100 cm³ of water was added 5.1 cm³ (5.8 g, 39 mmol) of TEA. The reaction flask was stirred for 19 h at room temperature, during which a white precipitate appeared. The precipitate was separated by filtration and was washed with 50 cm³ of ether, before being dried under vacuum. Water was removed from the filtrate using a rotatory evaporator and the remaining solid was washed with 100 cm³ of ether and then dried under vacuum. ^{1}H and ^{13}C NMR spectral analysis and a mp comparison showed that both products are essentially the same. This compound was recrystallized by cooling a refluxing methanol solution to room temperature. Yield: 89.1%. Mp: 181–183°C. ^{1}H NMR (D₂O) 4.67 (s, 6 H, OH), 3.73 (t, 12 H, $^{3}J_{HH}$ = 5.4 Hz, OCH₂), 3.30 (t, 12 H, $^{3}J_{HH}$ = 5.4 Hz, NCH₂). ^{13}C NMR (D₂O) 55.41 (OCH₂), 55.24 (NCH₂). MS (FAB), m/z 483 (M+H)⁺, 426 (M−Cl)⁺, 277 (M−Cl−TEA)⁺, 150 (TEA+H)⁺. IR (Nujol mull) 3400 (s,br), 3148 (w), 2919 (s), 2850 (s), 2723 (w), 2608 (w), 1486 (m), 1376 (m), 1300 (w), 1194

(w), 1093 (w), 1031 (m), 916 (m), 856 (w), 759 (w), 722 (w), 605 (m), 526 (m).

Preparation of Cd(TEA)₂(NO₃)₂ (8)

The procedure for the preparation of **8** is the same as that for **1** except that the reaction was done in ether. Large crystals suitable for X-ray crystallography were obtained by cooling a saturated refluxing methanol solution to room temperature. Yield: 92.0%. Mp: 221–222°C (dec). ^{1}H NMR (CD₃OD) δ 4.78 (s, 6 H, OH), 3.69 (t, 12 H, $^{3}J_{HH}$ = 5.4 Hz, OCH₂), 2.76 (t, 12 H, $^{3}J_{HH}$ = 5.4 Hz, NCH₂). ^{13}C NMR (CD₃OD) δ 57.66 (OCH₂), 56.32 (NCH₂); ^{113}Cd NMR (D₂O in H₂O, 0.05 M) δ −15.06, (CD₃OD in MeOH, 0.1 M) δ −33.43. MS (FAB). m/z 473 (M−NO₃)⁺, 324 (M−NO₃−TEA), 150 (TEA+H)⁺. IR (Nujol mull) 3312 (s, br), 2950 (s), 2920 (s), 2852 (s), 1731 (w), 1457 (m), 1315 (m), 1224 (w), 1061 (w), 1020 (m), 904 (m), 823 (w), 741 (w), 722 (w). Found: C, 26.9; H, 5.4. Calc for C₁₂H₃₀CdN₄O₁₂: C, 26.9; H, 5.7%.

Preparation of Pb(TEA)₂(CH₃CO₂)₂ (9)

The procedure for the preparation of this compound is the same as that for **3** except that MeOH was used as the solvent. Yield 97.0%. Mp: 116–118°C. ^{1}H NMR (CD₃OD) δ 4.78 (s, 6 H, OH), 3.66 (t, 12 H, $^{3}J_{HH}$ = 5.4 Hz, OCH₂), 2.71 (t, 12 H, $^{3}J_{HH}$ = 5.4 Hz, NCH₂), 1.70 (s, 12 H, CH₃CO₂). ^{13}C NMR (CD₃OD) δ 180.80 (CH₃CO₂), 59.86 (OCH₂), 58.20 (NCH₂), 25.02 (CH₃CO₂). MS (FAB), m/z 564 (M−CH₃CO₂)⁺, 505 (M−2CH₃CO₂+H)⁺, 266 (PbCH₃CO₂)⁺, 150 (TEA+H)⁺. IR (Nujol mull) 3100 (br,m), 2953 (s), 2851 (s), 2840 (w), 1573 (m), 1492 (m), 1377 (m), 1274 (m), 1140 (w), 1061 (w), 1021 (m), 893 (m), 817 (w), 739 (w), 656 (m).

Preparation of Bi(TEA)₂Cl₃ (10)

The procedure for the preparation of this compound is the same as that for **1** except that MeOH was used as the reaction solvent. The product was not soluble in a variety of solvents, thus precluding obtaining ^{1}H or ^{13}C NMR spectra in solution. Yield: 67.5%. Mp: 170–172°C (dec). ^{13}C CP/MAS spin rate 2.7 kHz) 55.93 (OCH₂ and NCH₂). MS (FAB) was not successful. IR (Nujol mull) 3278 (m, br), 2954 (s), 2849 (s), 2711 (w), 1405 (m), 1458 (s), 1377 (m), 1323 (w), 1231 (w), 1195 (w), 1094 (m), 1029 (w), 1003 (m), 916 (m), 899 (m), 722 (w), 604 (s), 535 (w), 528 (m).

Single crystal X-ray structures of **2** *and* **8**

A tetrahedral crystal of **2** and a monoclinic crystal of **8** were mounted on glass fibres which were placed on a Siemens P4RA and an Enraf–Nonius CAD4 diffractometer, respectively. Pertinent data collection and reduction information are given in Table 1. Important bond distances and angles for **2** and **8** are collected in Tables 2 and 3, respectively. The structures of **2** and **8** were solved by direct methods. The non-hydrogen atoms of both structures were refined anisotropically. All hydrogen atoms, with the exception of the hydroxyl protons, were modeled as riding atoms having a bond distance of 0.96 Å and refined with isotropic thermal parameters. The hydroxyl protons were refined isotropically until the final cycle of least squares. At this point the hydroxyl protons were converted to riding atoms in order to converge the refinement. All refinement calculations were performed on a Digital Equipment Micro VAX 3100 computer using the SHELXTL-Plus programs.[9]

DISCUSSION

The TEA complexes were synthesized by the reaction of TEA and the salt in a suitable solvent. These complexes are generally less soluble than their corresponding parent salts, and $Zn(TEA)_2Br_2$ and $Bi(TEA)_2Cl_3$ are not soluble in any common solvent. The new compounds were characterized by ^1H and ^{13}C NMR spectroscopy except for Fe (TEA)$_2$Cl$_3$ (**3**) which gave no useful information in

its ^1H NMR spectrum owing to its paramagnetic nature. The ^{13}C NMR spectrum revealed two somewhat broadened peaks for the OCH_2 and NCH_2 carbons.

The ^1H and ^{13}C NMR spectra of **1, 2** and **5–10** are simple and except for **2** and **9**, their ^1H NMR spectra show a singlet for the three OH groups of TEA as well as two triplets for the NCH_2 and OCH_2 protons. In the case of compound **2**, several peaks in the aromatic ^1H region were also observed corresponding to the presence of three molecules of pyridine. In the ^1H NMR of compound **9**, methyl protons of the acetate group were observed as a singlet at δ 1.70 ppm. The integration of the protons in the acetate group relative to those of the TEA ligands allows the conclusion that there are two TEA ligands per lead atom. Lacking crystals of **9** suitable for X-ray crystallography, however, the extent of TEA coordination in this compound is impossible to assess, especially in view of the fact that lead(II) possesses a potentially stereoactive lone pair. Except for compound **9**, ^{13}C NMR spectroscopy reveals separate resonances for the OCH_2 and NCH_2 carbons. The ^{13}C NMR spectrum of compound **2** also exhibits the presence of three molecules of Py. Interestingly, while the position of the NCH_2 peaks remains almost unchanged in these complexes relative to that in free TEA, the chemical shifts of the OCH_2 carbon generally moves upfield. Thus, the two carbon peaks are closer to each other in comparison to the free TEA, and in the case of $Bi(TEA)_2Cl_3$ (**9**) they coincide. FAB mass spectra for **1** and **3–9** show peaks corresponding to the

Table 1. Crystallographic data for **2** and **8**

	2	**8**
Formula	$C_{27}H_{45}Cl_3N_5O_{18}Y$	$C_{12}H_{30}CdN_4O_{12}$
M	922.9	534.8
Space group	*R*3	*C*2/c
a (Å)	14.901(2)	19.728(4)
b (Å)		8.753(2)
c Å)	15.255(3)	13.931(3)
α (°)		
β (°)		122.51(2)°
γ (°)		
V (Å^3)	2933.1(6)	2028.6(6)
Z	3	4
$\mu(Mo\ K_\alpha)$ (mm^{-1})	1.771	1.141
Data collec. instrument	Siemens P4RA	Enraf–Nonius CAD4
Temp (°C)	− 50	− 50
R^a	0.0347	0.0277
$R_w{}^b$	0.0418	0.0389

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

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

Bond lengths

Y—N	2.584(9)	Y—O	2.277(5)
Y—N'	2.785(10)	Y—O'	2.346(8)
Y—OA	2.277(4)	Y—O	2.277(2)
Y—O'A	2.346(6)	Y—O'	2.346(6)

Bond angles

N—Y—O	66.5(1)	O'—Y—OA	76.5(2)
O—Y—N'	113.5(1)	O—Y—O'	76.7(2)
O—Y—O'	76.7(2)	N—Y—N'	180.0(1)
O—Y—OA	105.1(2)	N—Y—O'	116.6(2)
O—Y—O'A	177.0(2)	N'—Y—O'	63.4(2)
O'—Y—O'A	101.6(2)		

Table 3. Selected bond distances (Å) and angles (°) for **8**

Bond lengths

Cd—N(1)	2.460(2)	Cd—O(1)	2.395(3)
Cd—O(2)	2.413(2)	Cd—O(3)	2.444(2)

Bond angles

N(1)—Cd—O(1)	72.0(1)	O(3)—Cd—O(3A)	73.8(1)
O(1)—Cd—O(2)	92.4(1)	Cd—N(1)—C(1)	109.7(2)
O(1)—Cd—O(3)	124.2(1)	N(1)—Cd—O(2)	68.2(1)
N(1)—Cd—N(1A)	167.5(1)	N(1)—Cd—O(3)	70.3(1)
O(2)—Cd—N(1A)	123.2(1)	O(2)—Cd—O(3)	109.5(1)
N(1)—Cd—O(1A)	110.3(1)	O(3)—Cd—N(1A)	99.4(1)
O(2)—Cd—O(1A)	71.2(1)	O(1)—Cd—O(1A)	160.1(1)
O(3)—Cd—O(2A)	163.9(1)	O(2)—Cd—O(2A)	71.9(1)
O(1)—Cd—O(3A)	73.5(1)	Cd—N(1)—C(3)	108.8(2)

cations as well as fragments. These experiments for **2** and **10** were not successful. Broad bands in the IR spectra of **2** and **10** at 3163 and 3278 cm^{-1}, respectively, show the presence of hydrogen bonding among the OH groups of TEA.

Since eight, nine and ten-coordinations are rather common for yttrium, and since the NMR spectra of **2** do not reveal whether the pyridines are metal coordinated or possibly hydrogen bonded to the OH of TEA,[2b] it was decided to further investigate the structure of this compound by X-ray crystallography. The structure of the cation of **2** is shown in Fig. 1, while Fig. 2 depicts the positions of the pyridines and ClO_4^- anions. The unit cell of **2** is shown in Fig. 3. In this interesting polar noncentrosymmetric crystal structure, yttrium(III) is octa-coordinated by the two ligating TEA groups. However, the pyridine molecules form hydrogen bonds (1.709 Å) with the hydroxyl protons on the unprimed side of the molecule while an
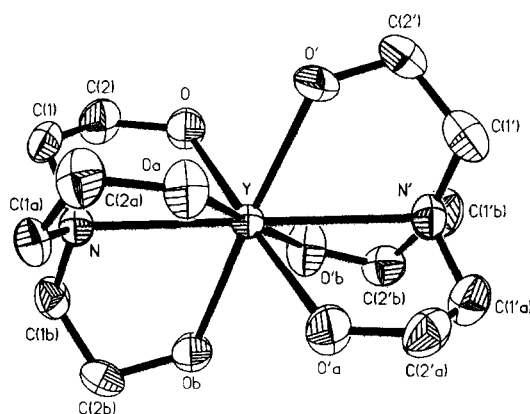

Fig. 1. ORTEP of the cation of **2**. The ellipsoids are drawn at the 50% probability level.

oxygen of each perchlorate forms a hydrogen bond (1.806 Å) with the hydroxyl protons on the primed side of the molecule. This separation of the charged
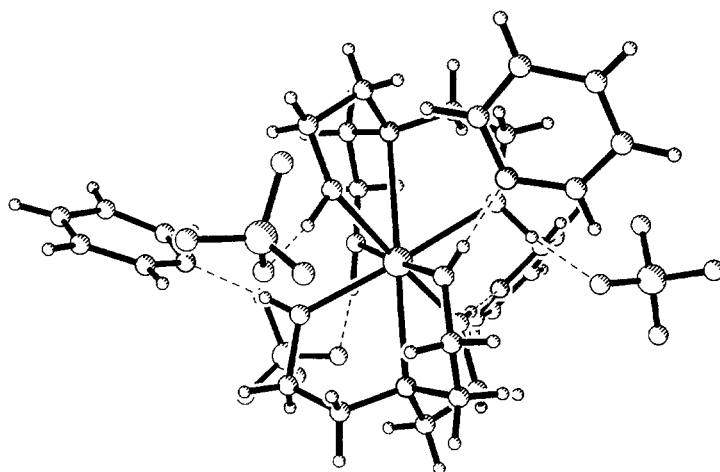
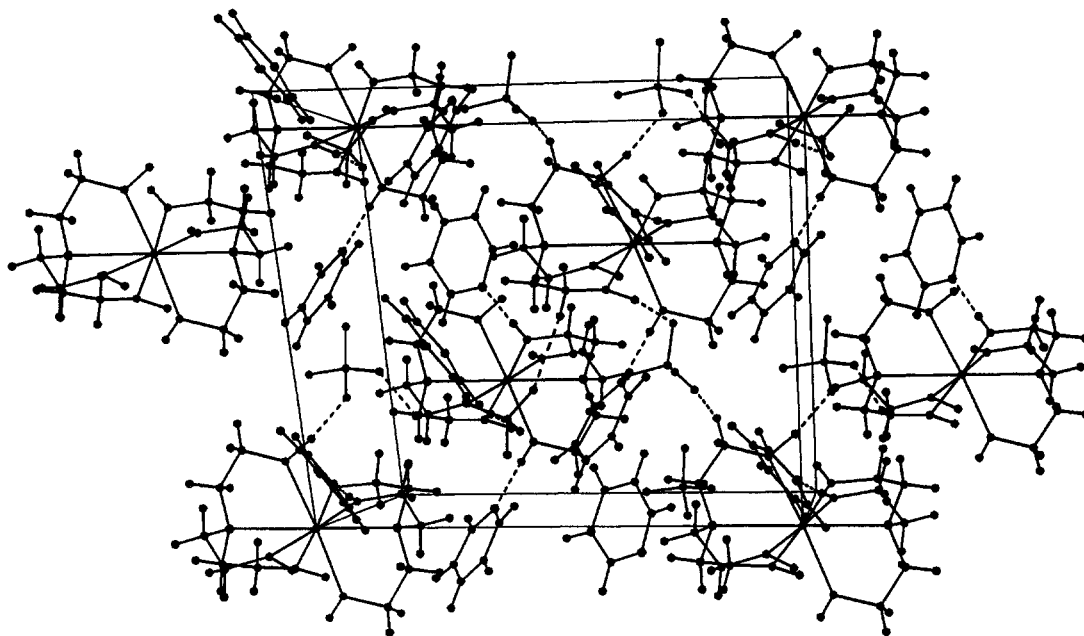Fig. 2. ORTEP of the cation of **2** showing the hydrogen bonding to a monomeric unit.

Fig. 3. Unit cell of **2**.

and uncharged hydrogen bonding ligands with respect to the cation may be responsible for the lengthening of the Y—N' bond relative to Y—N (2.584(9) to 2.785(10) Å) and the lengthening of the Y—O' bonds relative to the Y—O (2.277(4), to 2.346(6) Å).

The structures of $Ln(TEA)_3(CF_3SO_3)_3(THF)_3$ (Ln = Pr (**11**)) and Yb (**12**) have been recently reported.[5] In those molecules, one THF is coordinated to the metal, the second THF is hydrogen bonded to an OH group of TEA, and the third one is present as a solvent of crystallization.[5] While the metal in **2** is eight-coordinate, Ln in **11** and **12** is nine-coordinate. Moreover the M—O and M—N

distances involving the two TEA groups are different in **2** while they are very similar in **11** and **12**.

The average distance of 2.277(4) Å for Y—O in **2** is comparable with Y—μ_2-O distances reported for $Y_5(\mu_5$-O-i-Pr)$_4(\mu_2$-O-i-Pr)$_4$(O-i-Pr),[10] $Y_3(\mu_3$-O-t-Bu)$_3(\mu_3$-Cl)(μ_2-O-t-Bu)$_3$(O-t-Bu)$_4$(THF)$_2$,[11] [$Y_4(\mu_3$-O-t-Bu)$_2(\mu_2$-O-t-Bu)$_4$(O-t-Bu)(μ_4-O)(μ_2-Cl)Li$_4(\mu_2$-O-t-Bu)$_2]_2$[11] and $(C_5H_5)_5Y_5(\mu_2$-OMe)$_4(\mu_3$-OMe)$_4$ $(\mu_5$-O),[12] while the average Y—O' distance (2.346 (6) Å) is in the range of Y—μ_3-O bond lengths of these alkoxides. For comparison, the Y—O distances in Y_2O_3[13] and $UO_3 \cdot 3Y_2O_3$[14] are 2.28 and 2.305 Å, respectively.
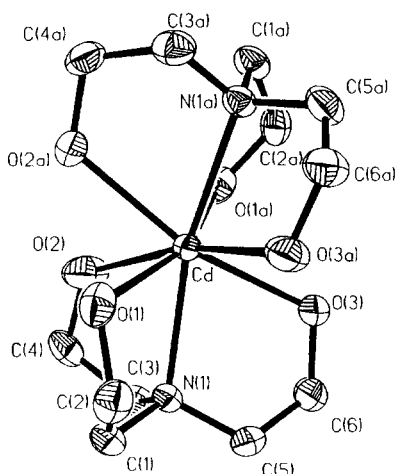
As a result of extensive hydrogen bonding

Fig. 4. ORTEP of the cation of **8**. The ellipsoids are drawn at the 50% probability level.

between the OH groups of TEA and the oxygen atoms of the perchlorate anions and the nitrogen atoms of pyridine, this compound has a three-dimensional polymeric structure (Fig. 3). Although extensive hydrogen bonding has also been observed in other complexes of TEA,[2-4] compound **2** represents the first example in which all the anions (when there is more than one per metal) as well as three molecules of solvent are hydrogen bonded to a monomeric unit (Fig. 2).

The ORTEP drawing of the cation of **8** is shown in Fig. 4 while the unit cell depiction is given in Fig. 5. Here cadmium is eight-coordinate as a result of ligation by two TEA groups. This coordination number is not common for cadmium,[15] and it has been structurally verified in only eight other

instances, all but one of them in complexes containing macrocyclic ligands.[16-21] In striking contrast to **2**, the M—O and M—N lengths for both TEA groups are almost equal in **8** as a result of similar hydrogen bonding between the OH groups of each TEA and the NO_3^- anions. The average Cd—O bond distance in **8** is 2.417(3) Å which closely matches that reported for [Cd(L)(NO$_3$)$_2$] (2.396 (3) Å) wherein cadmium is eight-coordinate and L = 1, 4, 7, 10-tetraoxa-13-azacyclopentadecane.[17] However, it is shorter than that in catena-bis(μ-6-amino-3-methyl, 5-nitrosouracilato-N[5], O[4], N[1], O[2])cadmium (2.625(2) Å) in which the cadmium is eight-coordinate.[16] The metal–oxygen distance in Cd$_9$(OC$_2$H$_4$OMe)$_{18}$·2HOC$_2$H$_4$OMe ranges from 2.129(6) Å to 2.555(6) Å.[22] The Cd—O distances in this cluster complex fall in the pattern Cd—O (terminal) $< \mu_2, \eta^1$-Cd—O $\cong \mu$-η^2-Cd—O $< \mu_3$-η^2-Cd—O $<$ Cd—O(ether). In **8** the average Cd—O distance lies between μ_2, η^1-Cd—O or μ-η^2-Cd—O and μ_3-η^2-Cd—O. The Cd—N bond in **8** is 2.460 (2) Å, which is only slightly longer than the Cd—O link. This is in striking contrast with the structure of **2** in which the average Y—N bond length is about 0.3 Å longer than the average Y—O distance. Noteworthy is the 167.6(1)° angle for the N(1)—Cd—N(1A) angle in **8** which contrasts that in centrosymmetric species such as the Sr(TEA)$_2^{2+}$ cation.[8b]

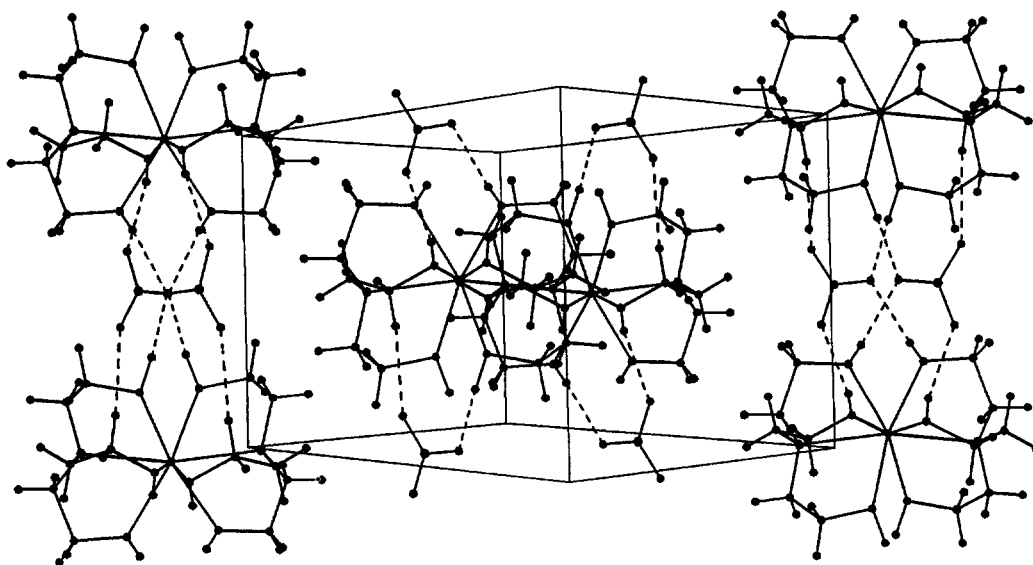Supplementary material available. Tables of crystal

Fig. 5. Unit cell of **8**.

data, bond distances, bond angles, hydrogen atom positional parameter, and general displacement parameter expressions (36 pages).

REFERENCES

1. (a) M. J. Hampden-Smith, T. A. Wark and C. Brinker, *J. Coord. Chem. Rev.* 1992, **112**, 81; (b) C. J. Brinker and G. Scherer, *Sol–Gel Science.* Academic Press, San Diego (1990).
2. (a) E. R. Myers and A. Kingon, *Ferroelectric Thin Films. Mat. Res. Soc. Proc.* 1990, 200; (b) K. M. Chi, H.-K. Shin, M. J. Hampden-Smith, E. N. Duesler and T. T. Kodas, *Polyhedron* 1991, **10**, 2293.
3. J. G. Verkade, *Acc. Chem. Res.* 1993, **26**, 483.
4. E. Jaffe, *Annall di Chimica Applicata* 1932, **22**, 737.
5. F. E. Hahn and J. Mohr, *Chem. Ber.* 1990, **123**, 481.
6. J. C. Voegele, J. Fischer and R. Weiss, *Acta Cryst.* 1974, **B30**, 62.
7. A. A. Naiini, J. Pinkas, W. Plass, V. Young and J. G. Verkade, *Inorg. Chem.* 1994, **33**, 2137.
8. (a) A. Taeb, H. Krishner and Ch. Kratky, *Z. Kristallogr.* 1986, **177**, 263; (b) J. C. Voegele, J. Fischer and R. Weiss, *Acta Cryst.* 1974, **B30**, 66; (c) J. C. Voegele, J. C. Thierry and R. Weiss, *Acta Cryst.* 1974, **B30**, 70; (d) J. A. Kanters, W. J. J. Smeets, K. Venkatasubramanian and N. S. Poonia, *Acta Cryst.* 1984, **C40**, 1701; (e) J. A. Kanters, A. deKoster, A. Schouten, K. Venkatasubramanian and N. S. Poonia, *Acta Cryst.* 1985, **C41**, 85.
9. SHELXTL-PLUS, Siemens Analytical X-ray Inc., Madison, WI.
10. O. Poncelet, W. J. Sartain, L. G. Hubert-Pfalzgraf, K. Folting and K. G. Caulton, *Inorg. Chem.* 1989, **28**, 263.
11. W. J. Evans, M. S. Sollberger and T. P. Hanusa, *J. Am. Chem. Soc.* 1988, **110**, 1841.
12. W. J. Evans and M. S. Sollberger, *J. Am. Chem. Soc.* 1986, **108**, 6095.
13. G. H. O'Connor and T. M. Valentine, *Acta Cryst. Sect. B* 1969, **B25**, 2140.
14. S. F. Bartram, *Inorg. Chem.* 1966, **5**, 749.
15. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Edn, p. 599. Wiley and Sons, New York (1988).
16. M. A. Romero, M. N. Moreno, J. Ruiz, M. P. Sanchez and F. Nieto, *Inorg. Chem.* 1986, **25**, 1498.
17. K. A. Byriel, K. R. Dunster, L. R. Gahan, C. H. L. Kennard, J. L. Latten, I. L. Swann and P. A. Duckworth, *Inorg. Chim. Acta* 1993, **205**, 191.
18. K. A. Adam, S. Donnelly, A. J. Leong, L. F. Lindoy, B. J. McCool, A. Bashall, M. R. Dent, B. P. Murphy, M. McPartin, D. E. Fenton and P. A. Tasker, *J. Chem. Soc. Dalton Trans.* 1990, 1635.
19. C. R. Paige and M. F. Richardson, *Can. J. Chem.* 1984, **62**, 332.
20. M. G. B. Drew, J. deO. Cabral, M. F. Cabral, F. S. Esho and S. M. Nelson, *J. Chem. Soc. Chem. Commun.* 1979, 1033.
21. H. Strasdeit and S. Pohl, *Z. Naturforsch.* 1988, **43b**, 1579.
22. (a) S. Boulmaaz, R. Papiernik, L. G. Hubert-Pfalzgraf, J. Vaissermann and J.-C. Daran, *Polyhedron* 1992, **11**, 1331; (b) S. C. Goel, M. A. Matchett, M. Y. Chiang and W. E. Buhro, *J. Am. Chem. Soc.* 1991, **113**, 1844.