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Isolation and Crystal Structure of a Six Coordinate Yttrium Trichloride Complex of ϵ-Caprolactone, $YCl_3(C_6H_{10}O_2)_3$

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It has recently been reported that yttrium and lanthanide alkoxide complexes generate extremely active, living, ring-opening polymerization systems with ϵ-caprolactone, $C_6H_{10}O_2$, to form polymers with low polydispersity.[1,2] Since caprolactone is readily polymerized by many metal complexes,[3] little information is available on the first few steps of the metal-mediated polymerization process. For example, it is not even known how caprolactone initially coordinates to the metal center.

We report here the first X-ray crystallographic data on a caprolactone complex of yttrium. This compound is also the first six-coordinate $YCl_3(solvate)_x$ complex to be reported. Solvated yttrium and lanthanide trichloride structures typically crystallize as tetrasolvated pentagonal bipyramidal $LnCl_3(L)_4$ complexes (e.g., $YCl_3(DME)_2$ (DME = dimethoxyethane),[4] $GdCl_3(DME)_2$,[5] $LnCl_3(THF)_4$ (Ln = Eu,[6] Nd[7]), $SmCl_3(DME)(THF)_2$,[8] and $EuCl_3(pyridine)_4$[9]) or as polymeric seven- or eight-coordinate species (e.g. $[YCl_3(TEG)(18\text{-crown-}6)]_n$[10] (TEG = triethyleneglycol) or $[(\mu\text{-}Cl)_3La(C_7H_8O_2)_2]_n$[11] ($C_7H_8O_2$ = 2,6-dimethyl-4-pyrone)). Only for the lanthanide 2,6-dimethyl-4-pyrone and hexamethylphosphoramide (HMPA) complexes $GdCl_3$(2,6-dimethyl-4-pyrone)$_3$[12] and $PrCl_3(HMPA)_3$[13] have six-coordinate structures been observed.

YCl_3 dissolves in caprolactone at room temperature to form a saturated solution which, upon slow evaporation, deposits well-shaped crystals of $YCl_3(C_6H_{10}O_2)_3$.[14] The complex crystallizes as a trisolvated six-coordinate *mer*-octahedral complex in which each caprolactone is coordinated as a monodentate ligand through its carbonyl oxygen, Figure 1.[15] Although the six-coordinate structure found in **1** is relatively rare for yttrium and the lanthanide trihalides,[4-11,16] no evidence for coordination of the ring oxygen atoms of the caprolactone ligands is observed, and the complex is only slightly distorted from a regular octahedral geometry. The angles between the donor atoms of the trans ligands are close to 180° (O–Y–O, 187.7 (1)°; O–Y–Cl, 177.9 (1)°; Cl–Y–Cl, 166.8 (1)°) and 8 of the 12 angles between cis ligands are within 2° of 90° (Table I).

The three chloride ligands adopt a meridonal geometry which mimics the T-shaped disposition of halides in seven-coordinate $LnCl_3(L)_4$ complexes.[4-11] In contrast, the octahedral alkoxides

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(14) In a glovebox under nitrogen, anhydrous YCl_3 was stirred for 36 h in ϵ-caprolactone (4 mL), which had been previously dried and degassed over sieves. Undissolved YCl_3 was removed by centrifugation, leaving a saturated solution of YCl_3 in caprolactone. X-ray quality crystals were formed upon slow evaporation of the caprolactone over several weeks. **1** does not dissolve in toluene. In THF it forms an insoluble material and free caprolactone. Anal. Calcd for $YC_{18}H_{30}O_6Cl_3$: Y, 16.53; Found: Y, 16.97.
(15) Crystal data for $YC_{18}H_{30}O_6Cl_3$: triclinic, $P\bar{1}$, a = 10.083 (1) Å, b = 11.706 (1) Å, c = 11.702 (1) Å, α = 60.071 (7)°, β = 81.274 (9)°, γ = 75.741 (8)°, V = 1159.4 (2) Å^3, Z = 2, D_{calcd} = 1.540 g cm^{-3}. A colorless crystal of approximate dimensions 0.33 × 0.40 × 0.50 mm was immersed in Paratone-D, mounted on a glass fiber and transferred to a Siemens R3m/V diffractometer equipped with a modified LT-1 apparatus. Collection of low temperature (168 K) intensity data was carried out by use of the θ–2θ scan technique with Mo Kα radiation ($2\theta_{max}$ = 55°). Data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. The structure was solved by Patterson methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Refinement of positional and anisotropic displacement parameters led to convergence with R_F = 4.00%, R_{wF} = 5.84%, and GOF = 0.87 for 253 variables refined against 4846 data with $|F_o| > 2.0\sigma(|F_o|)$.
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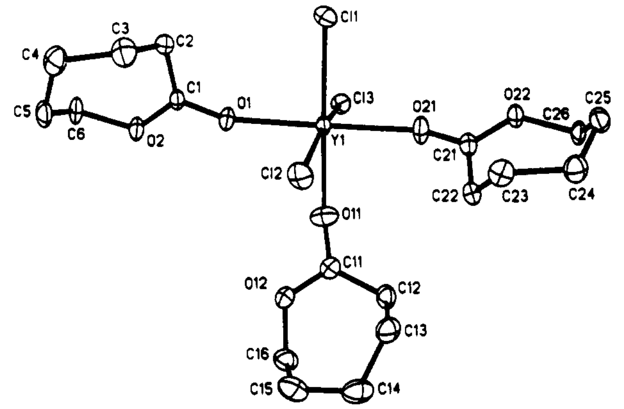

Figure 1. Molecular structure of $YCl_3(C_6H_{10}O_2)_3$ with probability ellipsoids drawn at the 50% level.

Table I. Selected Bond Distances (Å) and Angles (deg) for $YCl_3(C_6H_{10}O_2)_3$ (1)

Y(1)–Cl(1)	2.590 (1)	Y(1)–Cl(2)	2.574 (1)
Y(1)–Cl(3)	2.604 (1)	Y(1)–O(1)	2.274 (2)
Y(1)–O(11)	2.296 (3)	Y(1)–O(21)	2.269 (2)
O(1)–C(1)	1.233 (3)	O(11)–C(11)	1.229 (5)
O(21)–C(21)	1.226 (4)		
Cl(1)–Y(1)–Cl(2)	98.1 (1)	Cl(1)–Y(1)–Cl(3)	95.0 (1)
Cl(2)–Y(1)–Cl(3)	166.8 (1)	Cl(1)–Y(1)–O(1)	90.1 (1)
Cl(2)–Y(1)–O(1)	89.2 (1)	Cl(3)–Y(1)–O(1)	89.8 (1)
Cl(1)–Y(1)–O(11)	177.9 (1)	Cl(2)–Y(1)–O(11)	83.3 (1)
Cl(3)–Y(1)–O(11)	83.5 (1)	O(1)–Y(1)–O(11)	91.4 (1)
Cl(1)–Y(1)–O(21)	88.6 (1)	Cl(2)–Y(1)–O(21)	90.4 (1)
Cl(3)–Y(1)–O(21)	90.8 (1)	O(1)–Y(1)–O(21)	178.7 (1)
O(11)–Y(1)–O(21)	89.8 (1)	Y(1)–O(1)–C(1)	152.8 (2)
Y(1)–O(11)–C(11)	156.0 (2)	Y(1)–O(21)–C(21)	155.6 (2)

$Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$[17] and $Y(OSiPh_3)_3(THF)_3$[18] have a facial arrangement of the three anionic ligands. Interestingly, the closest crystallographically characterized analogs of **1**, the octahedral $GdCl_3$(2,6-dimethyl-4-pyrone)$_3$[12] and $PrCl_3(HMPA)_3$,[13] display both isomeric forms: the former has a facial arrangement, and the latter is meridonal.

The 2.574 (1)–2.604 (1)-Å Y–Cl distances in **1** are comparable to the analogous distances in seven-coordinate $[YCl_3(TEG)(18\text{-crown-}6)]_n$ (2.595 (3)–2.622 (2) Å)[10] and in seven-coordinate $YCl_3(DME)_2$ (2.597 (2)–2.603 (2) Å)[4] despite the difference in coordination number.[19] The 2.269 (2)–2.296 (3)-Å Y–O(caprolactone) distances in **1** are shorter than the 2.379 (3)–2.457 (3)-Å Y–O(DME) distances in $YCl_3(DME)_2$,[4] but they are longer than the 2.190-Å Y–O(antipyridine) distance in [Y(2,3-dimethyl-1-phenyl-pyrazolin-5-one)$_6$](I)$_3$.[20]

Several conclusions can be drawn from this structure. First, any mechanism proposed for the yttrium-mediated polymerization of caprolactone must consider that the caprolactone can initially bind as a monodentate ligand. Second, the predominance of seven and eight coordination in solvated yttrium and lanthanide trihalide complexes can be altered by choosing the proper coordinating ligand. Of course, this can be done with a very large ligand, but in this case it can be done with an oxygen donor that does not have an obviously large cone angle or three dimensional steric bulk. Finally, the ease of formation of **1** and the quality of the crystals suggest that, for those yttrium and lanthanide complexes which do not cause it to polymerize, caprolactone may be an excellent ligand for the preparation of crystalline materials in systems which do not readily crystallize with more common oxygen donor atom solvents.

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Supplementary Material Available: Tables of crystal data, positional parameters and isotropic thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom parameters (8 pages). Ordering information is given on any current masthead page.

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