ε-Caprolactam as a Donor Ligand for Lanthanide Halides: Formation of Cationic $[Ln(C_6H_{11}NO)_6Cl]^{2+}$ and $[Ln(C_6H_{11}NO)_4Cl_2]^{+}$ Complexes

William J. Evans,*[a] Cy H. Fujimoto,[a] Michael A. Greci,[a] and Joseph W. Ziller[a]

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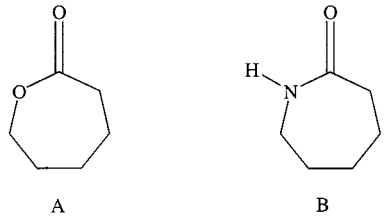
Examination of the coordination chemistry of ε-caprolactam with lanthanide trichlorides reveals that cationic ε-caprolactam-solvated complexes of two types can be obtained from acetonitrile depending on the size of the metal. The larger lanthanides Ce, Nd, Pr, and Sm form capped octahedral dications, $[Ln(C_6H_{11}NO)_6Cl]^{+2}$, with the chloride ligand in the capping position. The smaller metals Eu, Gd, and Ho form *trans*-octahedral monocations $[Ln(C_6H_{11}NO)_4Cl_2]^{+}$. Chloride ions are the counteranions in both cases.

Introduction

To define the first step in lanthanide-based ring opening polymerization of ε-caprolactone,[1] the coordination chemistry of this substrate with lanthanide trichlorides was previously studied.[2] These investigations showed that this monomer enhances the solubility of the lanthanide trichlorides in THF and generates a wide range of structures. $[YbCl_3(C_6H_{10}O_2)(THF)_2]$ and $[YCl_3(C_6H_{10}O_2)_3]$ were observed as well as ion pairs such as $[TbCl_4(THF)_2]^-[TbCl_2(THF)_5]^+$ and $[Cl_3Ln(\mu\text{-}Cl)_3LnCl_3]^{3-}$-$[Ln(C_6H_{10}O_2)_8]^{3+}$ (Ln = Sm and Nd).[2] This is in contrast to the usual coordination chemistry of yttrium and the lanthanide trichlorides in the presence of oxygen donors, which typically involves formation of seven coordinate pentagonal bipyramidal species of the general formula $LnCl_3L_4$ (L = oxygen donor ligand).[3]

Since metal trichlorides are important starting materials in the chemistry of yttrium and the lanthanides,[4] and since the presence of bridging or nonbridging ligands can have a significant effect on the chemistry of these metals,[5] it was of interest to determine if other neutral ligands similar to ε-caprolactone could likewise modify the chemistry of the lanthanide halides. Accordingly, we have studied the coordination chemistry of the lanthanide chlorides with a nylon-6 precursor, ε-caprolactam, since it is structurally similar to ε-caprolactone (Figure 1).



A B

Figure 1. A. ε-Caprolactone; B. ε-Caprolactam

[a] University of California, Irvine, Department of Chemistry, CA 92697−2025, USA
Fax: (internat.) +1-949/824-2210
E-mail: wevans@uci.edu

Since ε-caprolactam is more basic than ε-caprolactone, it has the potential to provide enhanced effects. To the best of our knowledge there is only one structural report of a lanthanide ε-caprolactam complex in the literature, $[Pr(C_6H_{11}NO)_8]^{3+}[OSO_2CF_3^-]_3$, a complex formed from hydrated praseodymium triflate and ε-caprolactam in triethylorthoformate.[6] We report here our synthetic and structural studies on the $LnCl_3$/ε-caprolactam system and the series of cationic complexes which resulted.

Results

ε-Caprolactam differs from ε-caprolactone[2] in that addition of this compound to slurries of the lanthanide trichlorides in THF does not bring the solids into solution. In fact, addition of ε-caprolactam to slurries of the lanthanide trichlorides in THF led to little visible change, except for the metals, neodymium, gadolinium, and holmium which had slight color changes. However, removal of solvent from these $LnCl_3$/ε-caprolactam mixtures, followed by washing with toluene to remove excess ε-caprolactam, gave solids whose IR spectra indicated the presence of coordinated ε-caprolactam. Crystallization from hot THF of the $PrCl_3$/ε-caprolactam product generated the dicationic ε-caprolactam complex $[Pr(C_6H_{11}NO)_6Cl]^{2+}$ as its chloride salt $[Pr(C_6H_{11}NO)_6Cl]Cl_2$ (Figure 2).

Single crystals of $[Ce(C_6H_{11}NO)_6Cl]Cl_2$ and $[Nd(C_6H_{11}NO)_6Cl]Cl_2$ were also obtained in this way, but the approach was not general for the remainder of the lanthanides.

Since THF was not a viable solvent for exploring the coordination chemistry of ε-caprolactam with the entire series of lanthanide trichlorides, an alternative solvent was examined. Acetonitrile proved to be suitable, even though it could have led to acetonitrile-solvated complexes. As with THF, addition of ε-caprolactam to slurries of lanthanide trichlorides in acetonitrile led to only small visible changes except for the Nd, Gd, and Ho systems. Although no obvious changes occurred, ε-caprolactam did become incorporated into the metal-containing solids isolated from these

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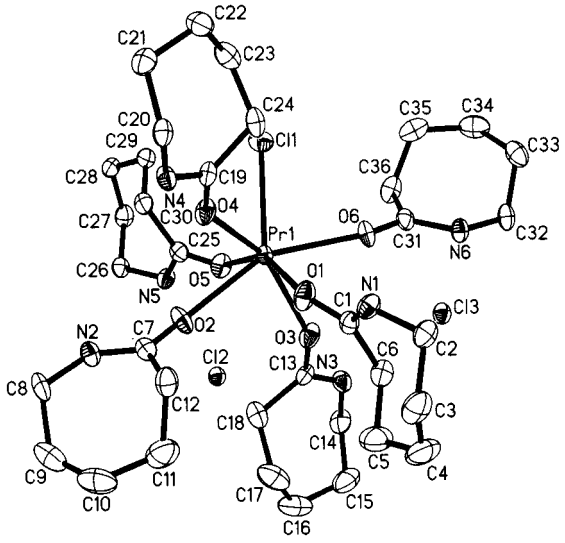

Figure 2. Thermal ellipsoid plot of $[Pr(C_6H_{11}NO)_6Cl)]Cl_2$ **(2)** with the probability ellipsoids drawn at the 50% level; complexes **1**, **3**, and **4** are isomorphous with **2**

systems. Recrystallization of these materials from hot acetonitrile gave single crystals suitable for X-ray diffraction for seven lanthanides ranging in size from Ce to Ho.

Two types of complexes crystallized, neither of which contained acetonitrile. Complexes of the formula $[Ln(C_6H_{11}NO)_6Cl]Cl_2$ (Figure 2) were found for the larger metals Ce **(1)**, Pr **(2)**, Nd **(3)**, and Sm **(4)**. Complexes **1, 2,** and **3** were identical to the ε-caprolactam complexes obtained from THF. Complexes of formula $[Ln(C_6H_{11}NO)_4Cl_2]Cl$ (Figure 3) were found for Eu **(5)**, Gd **(6)**, and Ho **(7)**.

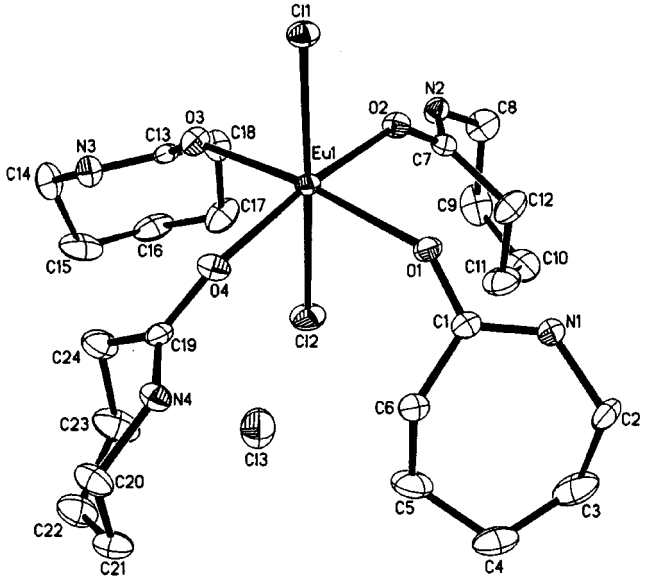

Figure 3. Thermal ellipsoid plot of $[Eu(C_6H_{11}NO)_4Cl_2)]Cl$ **(5)** with the probability ellipsoids drawn at the 50% level; complexes **6** and **7** are structurally similar to **5**

The complexes were characterized by infrared spectroscopy and elemental analysis and were definitively identified by X-ray crystallography. The IR spectra of **5−7** were similar to those of **1−4,** but the two types of spectra could be distinguished from each other in the fingerprint region. Single crystals were not obtained in the lanthanum case, **8**, but the white solid isolated from the analogous synthesis had an infrared spectrum identical to those of **1−4**.

Complexes **1−4** crystallize in the same space group and their unit cell parameters decrease from Ce to Sm, as is consistent with the decreasing size of the metals.[7] Each lanthanide in **1−4** is seven coordinate with a capped octahedral geometry arising from coordination of the carbonyl oxygen atoms of six ε-caprolactam molecules and one chloride, which is in the capping position. The two remaining chloride ions in the structure are separated from the metal at distances over 6 Å. The bond lengths in **1−3** and **5** vary as expected based on the changes in metal size (Table 1).

Only the praseodymium complex **2** will be described in detail since it can be directly compared to the only other lanthanide ε-caprolactam complex in the literature, $[Pr(C_6H_{11}NO)_8]^{3+}[OSO_2CF_3^-]_3$ **(9)**.[6] The degree of distortion in the capped octahedral geometry of **2** can be evaluated from the O−Pr−O angles between the *trans* oxygen atoms of the distorted octahedron, which range from 150.4−153.1(10)° and the adjacent O−Pr−O angles which range from 72.2(2)° to 117.8(2)° with an average angle of 87.6(2)°. The Pr−Cl distance [2.757(2) Å] can be compared to that in the six coordinate analog $PrCl_3(HMPA)_3$ [2.72(1) Å].[8] The average Pr−O bond length in **2** [2.418(3) Å] is comparable to that in **9** [2.449(12) Å] which has a higher coordination number and a higher charge on the cation. Both of these Pr−O(ε-caprolactam) distances are comparable to the Pr−O(HMPA) distance in $PrCl_3(HMPA)_3$ [2.353(2) Å],[8] a complex that also contains a strongly coordinating ligand.

The late metal complexes of formula $[Ln(C_6H_{11}NO)_4Cl_2]Cl$ [Ln = Eu **(5)**; Gd **(6)**; Ho **(7)**] have a six coordinate octahedral geometry with the chloride ligands in the *trans* positions. Complexes **6** and **7** are structurally similar to **5**, but they are not isomorphous. Unfortunately, only connectivity could be determined for both **6** and **7**, so **5** will be described in detail. The structure of **5** is only slightly distorted from a regular octahedral geometry with O−Eu−O *trans* angles of 172.42(7)−177.63(2)° and O−Eu−O *cis* angles of 85.17(5)−94.99(5)°. The Eu−Cl bond length in **5** [2.6505(8) Å] is comparable to the analogous bond length in seven coordinate $EuCl_3(THF)_4$,[3c] [2.628(3) Å]. The Eu−O bond in **5** [2.315(2) Å], is significantly shorter than the Eu−O(THF) distance in $EuCl_3(THF)_4$ [2.435(7) Å],[3c] even when the difference in coordination number is taken into account.[7]

Discussion

ε-Caprolactam differs considerably in its coordination chemistry with the lanthanide trichlorides compared to ε-caprolactone. Although its size and coordination mode, through the carbonyl group, are similar to those of ε-caprolactone, ε-caprolactam does not enhance the solubility of

Table 1. Bond lengths in $[Ln(C_6H_{11}NO)_6Cl]^{2+}$ and $[Ln(C_6H_{11}NO)_4Cl_2]^+$

Compound	Ln	Ln−O	$Ln-Cl_{coordinated}$	(Ln−O) − (Ln radius)[7]	(Ln−Cl) − (Ln radius)[7]
1	Ce	2.437(3)	2.7798(9)	1.37	1.71
2	Pr	2.418(3)	2.757(2)	1.36	1.70
3	Nd	2.407(3)	2.7412(12)	1.36	1.70
5	Eu	2.315(18)	2.6505(8)	1.37	1.71

the metal trichlorides and does not generate a variety of different structures upon coordination. Instead, the greater basicity of ε-caprolactam makes it such a powerful ligand that it displaces one or two chloride ligands from the metal and forms cationic complexes. The formation of these cations explains why ε-caprolactam does not increase solubility in solvents of moderate polarity.

The displacement of chloride ligands by ε-caprolactam leads to two types of crystalline cations, dicationic $[Ln(C_6H_{11}NO)_6Cl]^{2+}$ complexes for the larger metals and monocationic $[Ln(C_6H_{11}NO)_4Cl_2]^+$ compounds for the smaller metals. The existence of just two classes of compounds is typical of many types of lanthanide complexes in which the structural type with a high coordination number is found early in the series and a smaller coordinate variation forms with the later metals.[9]

Conclusion

Although ε-caprolactam is not useful in solubilizing lanthanide trichlorides, it is a powerful coordinating ligand which can displace anionic ligands and stabilize cationic complexes of these large metals.

Experimental Section

All of the compounds described below were handled under nitrogen with rigorous exclusion of air and water using standard Schlenk, vacuum line, and glovebox techniques. Solvents were prepared and physical measurements obtained as previously described.[10] All solvents were dried by distillation from sodium/benzophenone ketyl, except acetonitrile which was purchased anhydrous from Aldrich. ε-Caprolactam was purchased from Aldrich and sublimed before use. The lanthanide trichlorides were dried as previously described.[11] IR spectra were obtained as thin films using an ASI ReactIR 1000 spectrometer. Complete elemental analyses were performed by Desert Analytics, Tucson, Arizona. Complexometric analyses were obtained as previously described.[12]

General Procedures for the Synthesis of $[Ln(C_6H_{11}NO)_6Cl]Cl_2$ and $[Ln(C_6H_{11}NO)_4Cl_2]Cl$. Preparation of $[Ce(C_6H_{11}NO)_6Cl]Cl_2$ (1): In a glovebox, ε-caprolactam (0.36 g, 3.2 mmol) was added to a 15 mL slurry of THF and $CeCl_3$ (0.10 g, 0.41 mmol). After stirring overnight, volatiles were removed by rotary evaporation and the solids were washed with hot toluene (3 × 5.0 mL) to remove any excess ε-caprolactam. The resultant solid was dried under vacuum and was isolated as a white powder (0.20 g, 53%). X-ray quality crystals were grown from a concentrated THF solution. − $Ce(C_6H_{11}NO)_6Cl_3$ (925.43): calcd. C 46.72, H 7.19, N 9.08, Cl 11.49; found C 46.88, H 7.19, N 9.16, Cl 11.28. − IR: $\tilde{\nu}$ = 3177 vs, 2922 s, 2853 s, 1613 vs, 1490 s, 1440 s, 1351 s, 1293 s, 1258 s, 1200 s, 1119 s, 1079 s, 980 s, 822 s, 791 s, 690 s cm^{-1}. Complex **1** was also obtained using an analogous procedure with acetonitrile in place of THF. The composition of the product obtained from acetonitrile was determined by comparing IR spectra and unit cell parameters of single crystals.

$[Ln(C_6H_{11}NO)_6Cl]Cl_2$ [Ln = Pr (2); Nd (3); Sm (4)] and $[Ln(C_6H_{11}NO)_4Cl_2]Cl$ [Ln = Eu (5); Gd (6); Ho (7)]: Compounds **2**−**7** were prepared as described for **1**. Complexes **1**, **2** and **3** gave single crystals in THF and acetonitrile. Complexes **4**−**7** gave single crystals only from acetonitrile. Solvents, reagents, yields and spectroscopic data for individual samples are given below.

$[Pr(C_6H_{11}NO)_6Cl]Cl_2$ (2): In THF, $PrCl_3$ (0.09 g, 0.4 mmol) and ε-caprolactam (0.30 g, 2.7 mmol) were combined and a green solid (0.26, 77%) was isolated. − $Pr(C_6H_{11}NO)_6Cl_3$ (926.23): calcd. Pr 15.21, found Pr 15.0. − IR: $\tilde{\nu}$ = 3177 vs, 2922 s, 2853 s, 1613 vs, 1490 s, 1440 s, 1417 w, 1366 s, 1293 w, 1258 w, 1200 s, 1119 s, 1092 w, 1073 w, 980 s, 868 w, 826 s, 775 s, 690 s cm^{-1}.

$[Nd(C_6H_{11}NO)_6Cl]Cl_2$ (3): ε-Caprolactam (0.60 g, 5.3 mmol) was added to a pale blue-green slurry of $NdCl_3$ (0.17 g, 0.67 mmol) in THF and a light blue solid was isolated (0.42, 67%). − $Nd(C_6H_{11}NO)_6Cl_3$ (929.56): calcd. Nd 15.51, found Nd 15.2. − IR: $\tilde{\nu}$ = 3181 vs, 2922 s, 2853 s, 1610 vs, 1490 s, 1440 s, 1366 s, 1289 s, 1258 s, 1200 s, 1119 s, 1092 w, 1073 w, 980 w, 891 w, 868 w, 826 s, 772 s, 690 s cm^{-1}.

$[Sm(C_6H_{11}NO)_6Cl]Cl_2$ (4): $SmCl_3$ (0.1 g, 0.4 mmol) and ε-caprolactam (0.31 g, 2.7 mmol) were combined in acetonitrile. A white solid (0.29, 80%) was isolated. − $Sm(C_6H_{11}NO)_6Cl_3$ (935.68): calcd. Sm 16.07, found Sm 15.8. − IR: $\tilde{\nu}$ = 3176 vs, 2912 s, 2850 s, 1610 vs, 1487 s, 1438 s, 1417 w, 1366 s, 1293 w, 1258 w, 1200 s, 1119 s, 1092 w, 1073 w, 980 s, 868 w, 826 s, 775 s, 690 s cm^{-1}.

$[Eu(C_6H_{11}NO)_4Cl]Cl_2$ (5): ε-Caprolactam (0.50 g, 4.4 mmol) was added to a slurry of $EuCl_3$ (0.23 g, 0.89 mmol) in acetonitrile . The slurry was stirred overnight and was worked up as described above (0.35 g, 55%). − $Eu(C_6H_{11}NO)_4Cl_3$ (710.96): calcd. Eu 21.37, found Eu 21.5. − IR: $\tilde{\nu}$ = 3177 vs, 2922 s, 2853 s, 1617 vs, 1490 s, 1436 vs, 1200 s, 1119 s, 1089 s, 980 s, 961 s, 822 s, 791 s, 691 s cm^{-1}.

$[Gd(C_6H_{11}NO)_4Cl]Cl_2$ (6): ε-Caprolactam (0.51 g, 4.5 mmol) was added to a white slurry of $GdCl_3$ (0.22 g, 0.83 mmol) in acetonitrile. Immediately after mixing the reagents, a clear solution formed. After approximately 30 min., the mixture deposited a white precipitate. The resultant white solid was isolated as described above and dried under vacuum (0.51 g, 85%). − $Gd(C_6H_{11}NO)_4Cl_3$ (716.25): calcd. Gd 21.96; found Gd 21.4. − IR: $\tilde{\nu}$ = 3165 vs, 2930 s, 2860 s, 1606 vs, 1494 s, 1370 s, 1324 s, 1289 s, 1204 s, 1166 w, 1123 s, 1092 s, 984 s, 961 s, 892 w, 869 s, 826 s, 799 s, 691 s cm^{-1}.

$[Ho(C_6H_{11}NO)_4Cl_2]Cl$ (7): ε-Caprolactam (1.0 g, 8.9 mmol) was added to a pink slurry of $HoCl_3$ (0.44 g, 1.6 mmol) in acetonitrile. A white solid resulted (1.0 g, 85%). − $Ho(C_6H_{11}NO)_4Cl_3$ (723.93):

calcd. Ho 22.78; found Ho 22.0. − IR: $\tilde{\nu}$ = 3165 vs, 2926 s, 2860 s, 1606 vs, 1494 s, 1432 s, 1355 s, 1289 s, 1262 w, 1166 w, 1119 s, 1092 w, 1027 w, 984 w, 961 w, 891 w, 868 w, 822 s, 787 s, 687 s cm^{-1}.

$[La(C_6H_{11}NO)_6Cl]Cl_2$ (8): ε-Caprolactam (1.2 g, 11 mmol) was added to a white slurry of $LaCl_3$ (0.38 g, 1.6 mmol) in acetonitrile and the mixture was stirred overnight. The resultant solid was isolated following the procedures described above (0.53 g, 37%). − $La(C_6H_{11}NO)_6Cl_3$ (924.22): calcd. La 15.03; found La 15.4. − IR: $\tilde{\nu}$ = 3177 vs, 2922 s, 2853 s, 1602 vs, 1490 s, 1440 s, 1351 s, 1293 s, 1258 s, 1200 s, 1119 s, 1092 w, 1073 w, 980 s, 826 s, 776 s, 691 s cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for $[Ce(C_6H_{11}NO)_6Cl]Cl_2$ (1): A colorless crystal of approximate dimensions 0.15 × 0.14 × 0.13 mm obtained from a solution of acetonitrile was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[13] program package was used to determine the unit-cell parameters and for data collection (40 sec/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT[14] and SADABS[15] to yield the reflection data file. Details are in Table 2.

Subsequent calculations were carried out using the SHELXTL[16] program. The space group was the centrosymmetric monoclinic space group *Cc*. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[17] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, *wR2* = 0.0630 and GOF = 1.147 for 469 variables refined against 7697 unique data. As a comparison for refinement on *F*, *R1* = 0.0291 for those 7416 data with $I > 2\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.[18]

$[Pr(C_6H_{11}NO)_6Cl]Cl_2$ (2): All data were collected on a Siemens P4 diffractometer from a crystal of dimensions 0.43 × 0.43 × 0.40 mm. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out according to standard procedures. Intensity data were collected at 163 K using a 2θ/ω scan technique with Mo-K_α radiation. The raw data were processed with a local version of CARESS[19] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. Subsequent calculations were carried out using the SHELXTL[16] program. All data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The space group was the noncentrosymmetric *Cc*. At convergence, *wR2* = 0.0517 and GOF = 1.148 for 470 variables refined against all 5393 unique data. As a comparison for refinement of *F*, *R1* = 0.0218 for those 5152 data with $I > 2\sigma(I)$.

$[Nd(C_6H_{11}NO)_6Cl]Cl_2$ (3): From a solution of THF, a pale violet crystal of approximate dimensions 0.14 × 0.26 × 0.37 mm was mounted on a glass fiber and transferred to the Siemens P4 diffractometer. A total of 3995 intensity data within a limiting Bragg angle of 28.00° were measured. Structure solution and refinement were based upon all 3995 unique reflections. Solution of the structure was accomplished by a combination of direct and heavy-atom methods. Final full-matrix least-squares refinement of 469 structure parameters included anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in idealized positions (C−H = 0.96 Å) and refined by use of the riding model. Computer programs utilized included CARESS[19] for data processing and SHELXTL,[16] Version 5.02, for all other computations.

$[Eu(C_6H_{11}NO)_4Cl_2]Cl$ (5): A colorless crystal of approximate dimensions 0.07 × 0.25 × 0.31 mm was mounted on a glass fiber and handled as described above for **1**. The space group was the centrosymmetric monoclinic $P2_1/n$. At convergence, *wR2* = 0.0700 and GOF = 1.006 for 325 variables refined against 7304 unique data. As a comparison for refinement on F, *R1* = 0.0309 for those 5532 data with $I > 2\sigma(I)$.

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147969 (**3**), -147970 (**1**), -147971 (**2**), -147972 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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Table 2. X-ray crystallographic data for $[Ce(C_6H_{11}NO)_6Cl]Cl_2$ **(1)**, $[Pr(C_6H_{11}NO)_6Cl]Cl_2$ **(2)**, $[Nd(C_6H_{11}NO)_6Cl]Cl_2$ **(3)**, and $[Eu(C_6H_{11}NO)_4Cl_2]Cl$ **(5)**

Compound	**1**	**2**	**3**	**5**
Formula	$C_{36}H_{66}CeCl_3N_6O_6$	$C_{36}H_{66}Cl_3N_6O_6Pr$	$C_{36}H_{66}Cl_3N_6NdO_6$	$C_{24}H_{44}Cl_3EuN_4O_4$
M	925.42	926.21	929.54	710.94
Temp. (K)	158	168	163	158
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Cc*	*Cc*	*Cc*	$P2_1/n$
a (Å)	18.3538(10)	18.3487(14)	18.329(2)	12.0849(9)
b (Å)	10.5987(6)	10.5950(8)	10.5861(8)	20.8091(15)
c (Å)	23.4298(13)	23.401.(6)	23.398(2)	12.2285(9)
α (degrees)	90	90	90	90
β (degrees)	105.5350(10)	105.610(9)	105.638(5)	90.6580(10)
γ (degrees)	90	90	90	90
V ($Å^3$)	4391.2(4)	4381.5(12)	4371.9(6)	3075.0(4)
Z	4	4	4	4
$\rho_{calcd.}$ (Mg/m^3)	1.400	1.404	1.412	1.536
μ (mm^{-1})	1.266	1.342	1.418	2.334
Final *R*1[$I>2\sigma(I)$]	0.0290	0.0218	0.0234	0.0309
Final *wR*2 (all data)	0.0630	0.0517	0.0482	0.0700

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