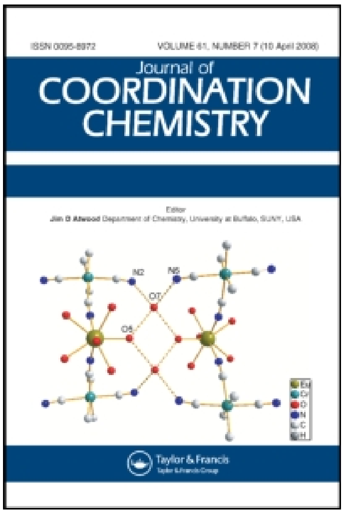

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COORDINATION CHEMISTRY OF N-METHYLIMIDAZOLE WITH YTTRIUM AND CERIUM

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COORDINATION CHEMISTRY OF N-METHYLIMIDAZOLE WITH YTTRIUM AND CERIUM

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YCl_3 crystallizes in the presence of N-methylimidazole (N-MeIm) to form $[YCl_2(N\text{-}MeIm)_5]^+[YCl_4(N\text{-}MeIm)_2]^-$, **1** or $[YCl_2(N\text{-}MeIm)_5]^+[Cl]^-$, **2**, depending upon crystallization conditions. The bromide analog of **2**, $[YBr_2(N\text{-}MeIm)_5]^+[Br]^-$, **3**, has been obtained from $YBr_3(THF)_3$ and N-MeIm. Both **1** and **2** contain seven coordinate pentagonal bipyramidal $[YCl_2(N\text{-}MeIm)_5]^+$ cations which have chloride atoms in the axial ligand positions. The anion in **1** has a *trans* octahedral geometry. Ceric ammonium nitrate crystallizes from N-MeIm to form $Ce(NO_3)_3(N\text{-}MeIm)_4$, **4**, which contains a formally ten-coordinate cerium center. **4** is best described as a seven coordinate distorted pentagonal bipyramid with the NO_3 ligands occupying one axial and two equatorial sites. **1** crystallized from N-MeIm in the space group P1 with $a = 8.1435\ (10)$ Å, $b = 9.0448(8)$ Å, $c = 15.103(2)$ Å, $\alpha = 93.872\ (10)^\circ$, $\beta = 94.117(11)^\circ$, $\gamma = 107.288(9)^\circ$, $V = 1054.8(2)$ Å^3 and $D_{calcd} = 1.520$ Mg/m^{-3} for $Z = 1$. Least squares refinement of the model based on 3375 reflections ($|F_0| > 2.0\sigma(|F_0|)$) converged to a final $R_F = 3.7\%$. **2** crystallized from a mixture of YCl_3 and trimethylaluminum in N-MeIm in the space group $P\bar{1}$ with $a = 9.462\ (3)$ Å, $b = 12.201\ (4)$ Å, $c = 13.087(4)$ Å, $\alpha = 77.53(3)^\circ$, $\beta = 73.13(2)^\circ$, $\gamma = 76.39(2)^\circ$, $V = 1387.5(7)$Å^3 and $D_{calcd} = 1.450$ Mg/m^{-3} for $Z = 2$. Least squares refinement of the model based on 3909 reflections ($|F_0| > 3.0\sigma(|F_0|)$) converged to a final $R_F = 4.7\%$. **3** crystallized from N-MeIm, was found to be isomorphous with **2** by a unit cell determination. **4** crystallized from a mixture of THF and N-MeIm in the space group $P2_1/n$ with $a = 9.9134(16)$ Å, $b = 18.967(3)$ Å, $c = 13.381(2)$ Å, $\beta = 90.864(12)^\circ$, $V = 2515.6(7)$ Å^3 and $D_{calcd} = 1.728$ Mg/m^{-3} for $Z = 4$. Least squares refinement of the model based on 5239 reflections ($|F_0| > 3.0\sigma(|F_0|)$) converged to a final $R_F = 3.9\%$.

KEYWORDS: cerium, yttrium, N-methylimidazole, lanthanide, ion pairs

INTRODUCTION

Recent studies of the coordination chemistry of lanthanide trihalides in the presence of oxygen donor solvents other than common ethers such as THF, dimethoxyethane, and Et_2O, have shown that these superficially simple LnX_3/solvent systems (where Ln = Y and the lanthanides, X = halides) display a surprisingly diverse structural chemistry. For example, while most LnX_3/ether systems

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crystallize as LnX_3(oxygen donor)$_4$ complexes,[1] lanthanide trichlorides in the presence of ε-caprolactone form the following: $YbCl_3(C_6H_{10}O_2)(THF)_2$, $YCl_3(C_6H_{10}O_2)_3$, $[TbCl_2(THF)_5]^+[TbCl_4(THF)_2]^-$ 1, $[Sm(C_6H_{10}O_2)_8]^{3+}$ $[Cl_3Sm(\mu\text{-}Cl)_3SmCl_3]^{3-}$, and $[Nd(C_6H_{10}O_{12})_8]^{3+}[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}$.[2,3] These structural variations are unusual and can have significant ramifications in reaction chemistry, because bridging ligands can have different reactivity than terminal ligands in lanthanide complexes[4,5] and cationic complexes show different chemistry than neutral or anionic species.[5,6] Since this means that certain donor solvents can influence the reaction rates of metal trihalides by the formation of ion pairs or bridged species, it is important to know the range of structural variations that are available for simple starting materials of the lanthanides in various solvents.

We have recently investigated the utility of N-methylimidazole, MeNCH = CHN = CH (N-MeIm) as a solvent in lanthanide chemistry and have found that, as in transition metal chemistry,[7–12] its strong ligating ability can provide some special opportunities in the coordination chemistry of the lanthanides. Our initial studies with N-MeIm involved divalent samarium halide starting materials.[13,14] In this report, we examine the effect of this solvent on typical Y(III) and Ce(IV) starting materials.

Experimental

All compounds described below were handled under nitrogen with rigorous exclusion of air and water using standard Schlenk, vacuum line and glove box techniques. THF was freshly distilled and dried as previously described.[15] Yttrium chloride (Rhône-Poulenc) was dried as previously described.[16] Yttrium bromide was prepared according to literature methods.[17] Ceric ammonium nitrate (Cerac) was dried under high vacuum at 65°C overnight and used without further purification. Redistilled N-methylimidazole (Aldrich, water content 0.013% by Analytische Laboratorien GmbH, D-51647 Gummersbach, Germany) and trimethylaluminum (Aldrich) were used without further purification.

$[YCl_2(N\text{-}MeIm)_5]^+[YCl_4(N\text{-}MeIm)_2]^-$, **1**

In a glovebox, anhydrous YCl_3 (0.50 g, 0.50 mmol) was stirred in THF (*ca.*2.0 mL) for 1 h and the solvent was removed by rotary evaporation. Most of the resulting white powder dissolved in N-MeIm (2.0 mL). After 2 days, the solution was decanted from the remaining precipitate and two drops of toluene were added to the soluble fraction. Crystals of **1** formed after 24 h.

$[YCl_2(N\text{-}MeIm)_5]^+[Cl]^-$, **2**

In a glovebox , $AlMe_3$ (1.0 mL, 10.7 mmol) was added via syringe to a stirred slurry of YCl_3 (0.07 g, 3.58 mmol) in hexanes. After 12 h, the mixture was dried by rotary evaporation and a white, THF insoluble powder was obtained. A slurry of this powder in N-MeIm was prepared, and after two weeks, crystals of **2** were isolated in nearly quantitative yield. *Anal* Calcd for $YC_{20}H_{30}N_{10}Cl_2$: Y, 14.68; C, 39.65; H, 4.99; N, 23.12; Cl, 17.56. Found: Y, 14.95; C, 39.52; H, 4.83; N, 22.95; Cl, 17.47.

$[(N\text{-}MeIm)_5YBr_2]^+[Br]^-$, 3

In a glovebox, $YBr_3(THF)_3$ (0.05 g, 0.92 mmol) was dissolved in N-MeIm (2.0 mL) to form a saturated solution. After two days, the solution was decanted off the remaining precipitate and two drops of toluene were added to the soluble fraction. **3** crystallized within 24 h and was found to be isomorphous with **2** by a unit cell determination.

$Ce(NO_3)_3(N\text{-}MeIm)_4$, 4

In a glovebox, ceric ammonium nitrate (0.50 g, 7.6 mmol) was dissolved in a 1:1 mixture of THF and N-MeIm (2.0 mL total) and stirred 12 h. Slow evaporation of the resulting viscous dark brown solution at ambient temperature deposited **4** as pale gold crystals after several days.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for 1, 2, and 4

In each case a crystal was immersed in Paratone-D oil under nitrogen and then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Syntex $P2_1$ diffractometer (Siemens R3m/V System) which is equipped with a modified LT-1 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out using standard techniques similar to those of Churchill.[18] Details are given in Table 1. All data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. Any reflection with $I(net) < 0$ was assigned the value $|F_0| = 0$. All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[19] or the SHELXTL PLUS program set.[20] The analytical scattering factors for neutral atoms were used throughout the analysis;[21] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_0|-|F_c|)^2$ where w^{-1} is defined below. The structures were refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C-H) = 0.96 Å and U(iso) = 0.08 $Å^2$ except where noted.

$[YCl_2(N\text{-}MeIm)_5]^+[YCl_4(N\text{-}MeIm)_2]^-$, 1

3599 data were collected on a colorless crystal of approximate dimensions 0.17 × 0.2 × 0.26 mm at 163 K. There were no systematic extinctions nor any diffraction symmetry other than the Freidel condition. The two possible triclinic space groups are the noncentrosymmetric $P1[C_1^1$; No. 1] or the centrosymmetric $P\bar{1}$ [C_i^1; No. 2]. Refinement of the model using the noncentrosymmetric space group proved it to be the correct choice. The quantity w^{-1} was defined as $\sigma^2(|F_0|) + 0.0005(|F_0|)^2$. The structure was solved by direct methods (SHELXTL PLUS); and refined by full-matrix least-squares techniques. There are two different independent molecules in the unit-cell. This is consistent with the observed Z-value of 1 for space group P1. Refinement of the model led to a convergence with $R_F = 3.7\%$, $R_{wF} = 3.7\%$ and GOF = 1.07 for 450 variables refined against those 3375 data with $|F_0| >$

$2.0\sigma(|F_0|)$. A final difference-Fourier map yielded $\rho(\max) = 0.47$ eÅ^{-3}. The absolute structure was determined by refinement of the Rogers' η-parameter.[22] Inversion of the model followed by least-squares refinement also indicated that the present model is correct ($R_F = 5.0\%$, $R_{wF} = 6.0\%$ and GOF = 1.73 for the inverted model).

Solution of the structure using the centrosymmetric space group was unsuccessful. In this space group, it would be necessary for each independent molecule to be located on an inversion center or for the unit-cell volume to be doubled. It is clear that the $[Y(N\text{-}MeIm)_5Cl_2]^+$ molecule does not possess the correct molecular symmetry to be located on an inversion center. Axial photographs confirmed the reported axial dimensions.

$[YCl_2(N\text{-}MeIm)_5]^+[Cl]^-$, 2

5216 data were collected on a colorless crystal of approximate dimensions 0.23 × 0.43 × 0.51 mm at 163 K. There were no systematic extinctions nor any diffraction symmetry other than the Freidel condition. The two possible triclinic space groups are the noncentrosymmetric $P1[C_1^1$; No. 1] or the centrosymmetric $P\bar{1}$ [C_i^1; No. 2]. Refinement of the model showed that the centrosymmetric space group was the correct choice. The quantity w^{-1} was defined as $\sigma^2(|F_0|) + 0.0009(|F_0|)^2$. The structure was solved by direct methods (SHELXTL PLUS); and refined by least-squares techniques. Refinement of the model led to a convergence with $R_F = 4.7\%$, $R_{wF} = 5.2\%$ and GOF = 1.10 for 308 variables refined against those 3909 data with $|F_0| > 3.0\sigma(|F_0|)$. A final difference-Fourier map yielded $\rho(\max) = 0.55$ eÅ^{-3}.

$Ce(NO_3)_3(N\text{-}MeIm)_4$, 4

6328 data were collected on a pale gold crystal of approximate dimensions 0.27 × 0.36 × 0.50 mm at 163 K. The diffraction symmetry was 2/m with systematic absences 0*k*0 for $k + 2n + 1$ and *h*0*l* for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c[C_{2h}^5$; No. 14] is therefore uniquely defined. The quantity w^{-1} was defined as $\sigma^2(|F_0|) + 0.0002(|F_0|)^2$. The structure was solved by direct methods (SHELXTL PLUS); and refined by least-squares techniques. Refinement of positional and thermal parameters led to a convergence with $R_F = 3.9\%$, $R_{wF} = 5.0\%$ and GOF = 2.23 for 335 variables refined against those 5239 data with $|F_0| > 3.0\sigma(|F_0|)$. A final difference-Fourier map yielded $\rho(\max) = 1.82$ eÅ^{-3} at a distance of 0.83 Å from Ce(1).

RESULTS AND DISCUSSION

Yttrium Trihalides with N-Methylimidazole

N-Methylimidazole (N-MeIm) dissolves THF-insoluble solids containing YCl_3 to form *two* types of N-MeIm solvated YCl_3 depending on crystallization conditions: $[YCl_2(N\text{-}MeIm)_5]^+[YCl_4(N\text{-}MeIm)_2]^-$, **1** (Figure 1), and $[YCl_2(N\text{-}MeIm)_5]^+[Cl]^-$, **2** (Figure 2). There are no close contacts between the cations and the anions in these complexes. $YBr_3(THF)_3$ crystallizes from N-MeIm to form $[YBr_2(N\text{-}MeIm)_5]^+[Br]^-$, **3**, which is isomorphous with **2**.

In each case, **1–3**, N-MeIm is a strong enough donor ligand to displace halide from the metal center. Complete displacement of halide ions from samarium by N-MeIm has been previously observed for SmI_3, which forms a compound containing an octasolvated trication, $[Sm(N\text{-}MeIm)_8{}^{3+}][I^-]_3$[13] and halide displacement is common in transition metal systems involving N-MeIm.[7–12,23–25] Loss of halide from a lanthanide with formation of an ion pair has also been observed in the $YbCl_3$/15-crown-5/$AlMe_3$ system which forms $[YbCl_2(15\text{-crown-}5)][AlMe_2Cl_2]$.[26] Formation of ion pairs under the proper conditions is well precedented in group 13 chemistry, *e.g.*, in $[AlCl_2(THF)_4][AlCl_4]$.[27]

Complexes **1–3** contain cationic components which have yttrium in a distorted pentagonal bipyramidal ligand environment with the halide ions in the axial positions. This type of structure has been observed in other seven coordinate cationic complexes of general formula $[LnZ_2(solvent)_5]^+$ (Z = monoanionic ligand) such as $[SmI_2(THF)_5]^+$,[28] $[YCl(OCMe_3)(THF)_5]^+$,[29] $[CeCl_2(THF)_5]^+$,[30] and $[TbCl_2(THF)_5]^+$.[3] The cations in **1** and **2** exhibit similar bond distances and angles as shown in Table 2. The Cl-Y-Cl angles of 174.0(1) and 174.5(1)°, in **1** and **2**, respectively, approach linearity and the Cl-Y-N(N-MeIm) angles cluster around the 90° angle of a regular pentagonal bipyramid with a range of 83.8(1)° to 97.8(2)°. The 72.2(18)° and 72.1(14)° average of the N-Y-N angles for adjacent imidazole ligands, in **1** and **2**, respectively, matches the 72° idealized angle and the 70.2(1)° to 75.4(2)° range of values is fairly narrow. As in $[SmI_2(THF)_5]^+$,[28] $[YCl(OCMe_3)(THF)_5]^+$,[29] and $[TbCl_2(THF)_5]^+$,[3] the five solvent molecules in **1** and **2** are canted in a propeller-like fashion around the metal center.

The average Y-Cl distances of 2.592(3) Å and 2.611(6) Å in **1** and **2**, respectively, are shorter than the 2.660(2) Å Y-Cl distance in $[YCl(OCMe_3)(THF)_5]^+$,[29] but are comparable to the 2.598(1) Å average Tb-Cl distance in $[TbCl_2(THF)_5]^+$(Tb^{3+} is 0.02 Å larger than Y^{3+}).[31] The ranges of Y-N(N-MeIm) distances, 2.462(6)–2.495(6) Å in the cation of **1** and 2.467(4)–2.478(4) Å in **2**, are very similar. The average Y(1)-N distances of 2.478(12) Å and 2.474(4) Å found in the cations of **1** and **2**, respectively, are longer than the 2.402(16) Å Tb-O(THF) distances in $[TbCl_2(THF)_5]^+$ after the difference in metallic radii is considered.[31] Previously, it has been observed that Ln-N(N-MeIm) distances are quite similar to Ln-O(THF) lengths in comparable lanthanide complexes.[14]

The geometry around the yttrium in the anion of **1** is that of a slightly distorted octahedron with the two THF molecules *trans* to each other. The bond angles between the donor atoms of the *cis* ligands are clustered around 90° with a range of 86.7(1)° to 91.5(2)°, and the angles between the *trans* ligands are nearly linear: Cl(3)-Y(2)-Cl(6), 178.7(1)°; Cl(4)-Y(2)-Cl(5), 178.1(1)°; N(11)-Y(2)-N(13), 176.4(2)°. The average Y(2)-Cl bond length is 2.616(14) Å, which is similar to the average Tb-Cl distance of 2.629(8) Å in $[TbCl_4(THF)_2]^-$[3]. Interestingly, the Y-Cl distances for *trans* chlorides Cl(4) and Cl(5) (2.632(2) and 2.628(2) Å), are statistically longer than the Y-Cl distances for *trans* chlorides Cl(3) and Cl(6) (2.602(2) and 2.600(2) Å), although the difference is not great. There is no obvious reason for this in the packing diagram of **1**. The average Y(2)-N bond length is 2.427(3) Å compared to a 2.478(11) Å average Y(1)-N distance in the seven coordinate cation.

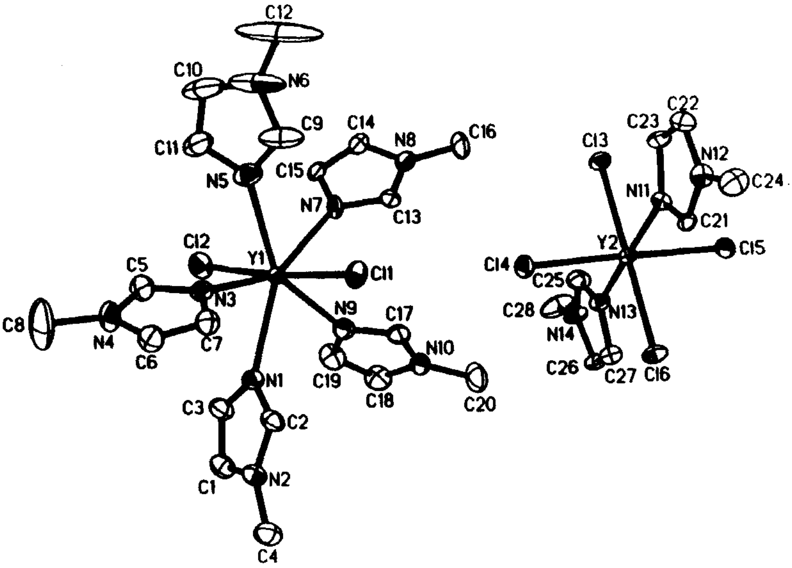

Figure 1 Thermal ellipsoid plot of $[YCl_2(N\text{-}MeIm)_5]^+[YCl_4(N\text{-}MeIm)_2]^-$, **1**, with probability ellipsoids drawn at the 50% level.

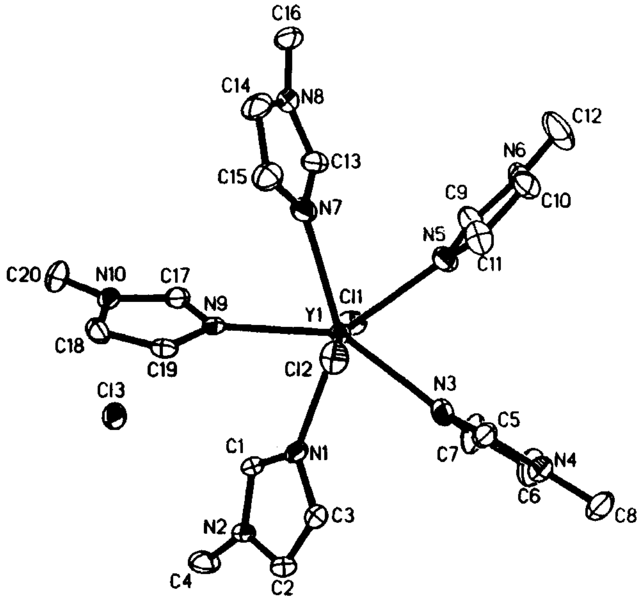

Figure 2 Thermal ellipsoid plot of $[YCl_2(N\text{-}MeIm)_5]^+[Cl]^-$, **2**, with probability ellipsoids drawn at the 50% level.

Table 1 Experimental data for the X-ray diffraction studies of $[YCl_2\ (N\text{-}MeIm)_5]^+$ $[YCl_4(N\text{-}MeIm)_2]^-$, **1**, $[YCl_2(N\text{-}MeIm)_5]^+[Cl]^-$, **2**, and $Ce(NO_3)_3(N\text{-}MeIm)_4$, **4**.

Compound	1	2	4
Formula	$[C_8H_{12}N_4Cl_4Y]$ $[C_{20}H_{30}Cl_2Y]$	$[C_{20}H_{30}N_{10}Cl_2Y]$ $[Cl]$	$C_{16}H_{24}N_{11}O_9Ce$
FW	965.3	605.8	654.6
Temp(K)	163	163	163
Crystal System	Triclinic	Triclinic	Monoclinic
Space Group	P1	PI	$P2_{1/n}$
a(Å)	8.1435(10)	9.462(3)	9.9134(16)
b(Å)	9.0448(8)	12.201(4)	18.967(3)
c(Å)	15.103(2)	13.087(4)	13.381(2)
α(deg)	93.872(10)	77.53(3)	
β(deg)	94.117(11)	73.13(2)	90.864(12)
γ(deg)	107.288(9)	76.39(2)	
Volume(Å^3)	1054.8(2)	1387.5(7)	2515.6(7)
Z	1	2	4
D_{calcd}(Mg/m^3)	1.520	1.450	1.728
Diffractometer	Syntex $P2_1$	Syntex $P2_1$	Syntex $P2_1$
Data Collected	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$	$+h, +k, \pm l$
Scan Type	Omega	Wyckoff	θ-2θ
Scan Range (deg)	1.20	2.00	1.2 plus Kα-separation
Scan Speed, deg min^{-1} (in ω)	4.0	30.0	3.0
2θ Range (deg)	4.0 to 48.0	4.0 to 50.0	4.0 to 55.0
μ(MoKα), mm^{-1}	3.175	2.432	1.768
Reflections Collected	3599	5216	6328
w^{-1}	$\sigma^2(\lvert F_0\rvert) +$ $0.0005(\lvert F_0\rvert)^2$	$\sigma^2(\lvert F_0\rvert) +$ $0.0009(\lvert F_0\rvert)^2$	$\sigma^2(\lvert F_0\rvert) +$ $0.0002(\lvert F_0\rvert)^2$
Refl with	X = 2	X = 3	X = 3
$(\lvert F_0\rvert > X\sigma(\lvert F_0\rvert))$	3375	3909	5239
No. of Variables	450	308	335
R_F, R_{wF}	3.7%, 3.7%	4.7%, 5.2%	3.9%, 5.0%
Goodness of Fit	1.07	1.10	2.23

Radiation: MoKα (λ = 0.710730 Å)
Monochomator: highly oriented graphite
Absorption Correction: semi-empirical (φ-scan method)

$(NH_4)_2\ Ce(NO_3)_6/N\text{-}MeIm$

N-methylimidazole is not a good donor solvent for the most common form of Ce(IV), namely ceric ammonium nitrate, since reduction to Ce(III) occurs upon mixing and the ammonium-free neutral Ce(III) complex $Ce(NO_3)_3(N\text{-}MeIm)_4$, **4** (Figure 3), is formed. However, isolation of **4** allows a comparison of N-MeIm and DME as solvating ligands using the previously studied structure of $Ce(NO_3)_3$ $(DME)_2$, **5**.[32] The structure of formally ten coordinate **4** is not easily described using common ten coordinate geometries.[33] However, if the small chelating nitrate groups are considered to occupy one coordination site, as is often done,[32,34-38] **4** can be viewed as a seven coordinate distorted pentagonal bipyramid in which N-MeIm N(6) and the nitrate containing N(3) are the apical ligands and the nitrate ligands containing N(1) and N(2) and the imidazole nitrogens, N(4), N(8), and N(10), comprise the ligands in the pentagonal plane. **5** can be viewed similarly with a

Table 2 Selected Bond Distances (Å) and Angles (°) for $[YCl_2(N\text{-}MeIm)_5]^+[YCl_4(N\text{-}MeIm)_2]^-$, **1**, $[YCl_2(N\text{-}MeIm)_5]^+[Cl]^-$, **2**, and $Ce(NO_3)_3(N\text{-}MeIm)_4$, **4**.

1		**2**		**4**	
Y(1)-Cl(1)	2.591(2)	Y(1)-Cl(1)	2.605(1)	Ce(1)-O(1)	2.615(3)
Y(1)-Cl(2)	2.593(3)	Y(1)-Cl(2)	2.616(1)	Ce(1)-O(2)	2.600(3)
Y(2)-Cl(3)	2.602(2)			Ce(1)-O(4)	2.638(3)
Y(2)-Cl(4)	2.632(2)			Ce(1)-O(5)	2.627(3)
Y(2)-Cl(5)	2.628(2)			Ce(1)-O(7)	2.764(3)
Y(2)-Cl(6)	2.600(2)			Ce(1)-O(8)	2.535(3)
Y(1)-N(1)	2.479(6)	Y(1)-N(1)	2.473(3)	Ce(1)-N(1)	3.027(4)
Y(1)-N(3)	2.469(7)	Y(1)-N(3)	2.478(4)	Ce(1)-N(2)	3.062(4)
Y(1)-N(5)	2.495(6)	Y(1)-N(5)	2.475(4)	Ce(1)-N(3)	3.082(4)
Y(1)-N(7)	2.462(6)	Y(1)-N(7)	2.477(4)	Ce(1)-N(4)	2.636(4)
Y(1)-N(9)	2.485(6)	Y(1)-N(9)	2.467(4)	Ce(1)-N(6)	2.669(3)
Y(2)-N(11)	2.431(7)			Ce(1)-N(8)	2.662(4)
Y(2)-N(13)	2.424(7)			Ce(1)-N(10)	2.603(3)
Cl(1)-Y(1)-Cl(2)	174.0(1)	Cl(1)-Y(1)-Cl(2)	174.5(1)	N(4)-Ce(1)-N(6)	81.8(1)
Cl(1)-Y(1)-N(1)	96.8(2)	Cl(1)-Y(1)-N(1)	85.8(1)	N(4)-Ce(1)-N(8)	74.7(1)
Cl(2)-Y(1)-N(1)	88.7(2)	Cl(2)-Y(1)-N(1)	90.7(1)	N(6)-Ce(1)-N(8)	83.0(1)
Cl(1)-Y(1)-N(3)	87.1(2)	Cl(1)-Y(1)-N(3)	91.2(1)	N(4)-Ce(1)-N(10)	143.3(1)
Cl(2)-Y(1)-N(3)	92.4(2)	Cl(2)-Y(1)-N(3)	83.8(1)	N(6)-Ce(1)-N(10)	91.8(1)
N(1)-Y(1)-N(3)	71.1(2)	N(1)-Y(1)-N(3)	74.5(1)	N(8)-Ce(1)-N(10)	140.5(1)
Cl(1)-Y(1)-N(5)	88.6(2)	Cl(1)-Y(1)-N(5)	90.0(1)	N(4)-Ce(1)-O(1)	73.7(1)
Cl(2)-Y(1)-N(5)	85.4(2)	Cl(2)-Y(1)-N(5)	90.6(1)	N(6)-Ce(1)-O(1)	115.2(1)
N(1)-Y(1)-N(5)	145.7(2)	N(1)-Y(1)-N(5)	146.0(1)	N(8)-Ce(1)-O(1)	140.4(1)
N(3)-Y(1)-N(5)	75.4(2)	N(3)-Y(1)-N(5)	71.9(1)	N(10)-Ce(1)-O(1)	76.7(1)
Cl(1)-Y(1)-N(7)	86.4(2)	Cl(1)-Y(1)-N(7)	90.8(1)	N(4)-Ce(1)-O(2)	74.9(1)
Cl(2)-Y(1)-N(7)	90.7(2)	Cl(2)-Y(1)-N(7)	94.5(1)	N(6)-Ce(1)-O(2)	67.2(1)
N(1)-Y(1)-N(7)	143.2(2)	N(1)-Y(1)-N(7)	142.4(1)	N(8)-Ce(1)-O(2)	139.9(1)
N(3)-Y(1)-N(7)	145.6(2)	N(3)-Y(1)-N(7)	143.1(1)	N(10)-Ce(1)-O(2)	69.4(1)
N(5)-Y(1)-N(7)	70.8(2)	N(5)-Y(1)-N(7)	71.2(1)	O(1)-Ce(1)-O(2)	48.8(1)
Cl(1)-Y(1)-N(9)	86.4(2)	Cl(1)-Y(1)-N(9)	93.5(1)	N(4)-Ce(1)-O(4)	141.0(1)
Cl(2)-Y(1)-N(9)	97.8(2)	Cl(2)-Y(1)-N(9)	89.4(1)	N(6)-Ce(1)-O(4)	115.6(1)
N(1)-Y(1)-N(9)	70.8(2)	N(1)-Y(1)-N(9)	72.7(1)	N(8)-Ce(1)-O(4)	73.3(1)
N(3)-Y(1)-N(9)	140.2(2)	N(3)-Y(1)-N(9)	146.4(1)	N(10)-Ce(1)-O(4)	74.0(1)
N(5)-Y(1)-N(9)	143.5(2)	N(5)-Y(1)-N(9)	141.3(1)	O(1)-Ce(1)-O(4)	121.2(1)
N(7)-Y(1)-N(9)	72.8(2)	N(7)-Y(1)-N(9)	70.2(1)	O(2)-Ce(1)-O(4)	143.3(1)
Cl(3)-Y(2)-Cl(4)	90.2(1)			N(4)-Ce(1)-O(5)	135.9(1)
Cl(3)-Y(2)-Cl(5)	90.4(1)			N(6)-Ce(1)-O(5)	67.3(1)
Cl(4)-Y(2)-Cl(5)	178.1(1)			N(8)-Ce(1)-O(5)	71.1(1)
Cl(3)-Y(2)-Cl(6)	178.7(1)			N(10)-Ce(1)-O(5)	70.9(1)
Cl(4)-Y(2)-Cl(6)	88.8(1)			O(1)-Ce(1)-O(5)	147.5(1)
Cl(5)-Y(2)-Cl(6)	90.6(1)			O(2)-Ce(1)-O(5)	116.9(1)
Cl(3)-Y(2)-N(11)	87.7(2)			O(4)-Ce(1)-O(5)	48.5(1)
Cl(4)-Y(2)-N(11)	91.5(1)			N(4)-Ce(1)-O(7)	111.6(1)
Cl(5)-Y(2)-N(11)	90.3(1)			N(6)-Ce(1)-O(7)	163.3(1)
Cl(6)-Y(2)-N(11)	91.5(2)			N(8)-Ce(1)-O(7)	109.6(1)
Cl(3)-Y(2)-N(13)	90.2(2)			N(10)-Ce(1)-O(7)	71.5(1)
Cl(4)-Y(2)-N(13)	91.4(1)			O(1)-Ce(1)-O(7)	62.2(1)
Cl(5)-Y(2)-N(13)	86.7(1)			O(2)-Ce(1)-O(7)	105.6(1)
Cl(6)-Y(2)-N(13)	90.6(2)			O(4)-Ce(1)-O(7)	60.0(1)
N(11)-Y(2)-N(13)	176.4(2)			O(5)-Ce(1)-O(7)	105.6(1)
				N(4)-Ce(1)-O(8)	73.0(1)
				N(6)-Ce(1)-O(8)	148.7(1)
				N(8)-Ce(1)-O(8)	72.8(1)
				N(10)-Ce(1)-O(8)	119.5(1)
				O(1)-Ce(1)-O(8)	75.6(1)
				O(2)-Ce(1)-O(8)	121.4(1)
				O(4)-Ce(1)-O(8)	76.5(1)
				O(5)-Ce(1)-O(8)	120.4(1)
				O(7)-Ce(1)-O(8)	48.0(1)

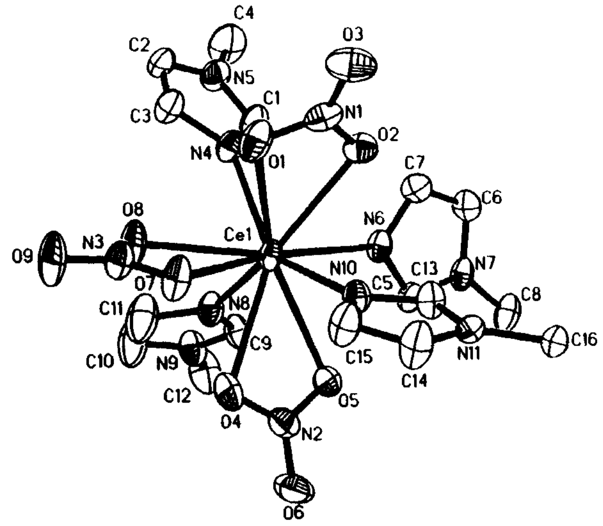

Figure 3 Thermal ellipsoid plot of $Ce(NO_3)_3(N\text{-}MeIm)_4$, **4**, with probability ellipsoids drawn at the 50% level.

nitrate in one apical position and a solvent donor atom in the other position. The structures of **4** and **5** differ however in the arrangement of ligands in the pentagonal plane: in **5**, the equatorial nitrate ligands are adjacent whereas in **4** they are not. The 172.8° N(3)-Ce(1)-N(6) angle in **4** approaches the 180° angle of a pentagonal bipyramid and the mean deviation of N(1), N(2), N(4), N(8), and N(10) from the plane of Ce is 0.065 Å.

The bond distances and angles of the bidentate nitrate ligands in **4** (Table 2) are not unusual[33] and are similar to those in **5**.[32] The O-Ce-O angles are 48.0(1), 48.5(1), and 48.8(1)° compared to 49.5(1), 49.9(1), and 49.9(1)° in **5**. The N-O distances for the oxygen atoms attached to cerium fall in a range of 1.250(5) to 1.288(5) Å, compared to 1.264(4)-1.277(4) Å in **5**. The other N-O distances are 1.213(5) to 1.229(5) Å in **4** compared to 1.218(3)-1.225(4) Å in **5**.[30] The O-N-O angles for the oxygen atoms connected to cerium are 116.6(3)–117.0(3)°, whereas the other O-N-O angles are 119.4(4)–123.6(4)°.

The average Ce-O distance of 2.63(7) Å in **4** is in the range of previously observed Ce-O(nitrate) average values: 2.569(15) Å in $[Ph_3EtP]_2[Ce(NO_3)_5]$,[37] 2.64(2) Å in $[Ce(NO_3)_6]_2Mg_3(H_2O)_{24}$,[39] 2.666 Å in $[Ce(NO_3)_4(H_2O)_2(4,4'\text{-bipyridine})]^-$,[40] and 2.57(3) Å in **5**.[32] The average Ce-N(N-MeIm) distance of 2.64(3) Å is similar to the average Ce-O(DME) distance of 2.57(3) Å in **5**, within the error limits.[32] The average Ce-N(N-MeIm) distance is also statistically similar to the Y-N(N-MeIm) distances in **1** and **2** when the differences in metallic radii and coordination number are considered.[31]

Conclusion

N-MeIm functions as a strong donor solvent for lanthanide complexes. It is comparable to common ethers in steric factors, as shown by the similarity of **1** and

2 to $[TbCl_2(THF)_5]^+[TbCl_4(THF)_2]^-$,[3] and the close resemblance of the structures of **4** and **5**. However, it can dissolve materials insoluble in THF and displace halide and THF ligands from the lanthanide metal ions. In this regard, N-MeIm offers opportunities to vary in significant ways the solubility and coordination environments of lanthanide complexes. N-MeIm is not a suitable ligand for nitrate-ligated Ce(IV), however, due to the redox chemistry which occurs.

SUPPLEMENTARY MATERIAL

X-ray diffraction and structure factor tables available from WJE.

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