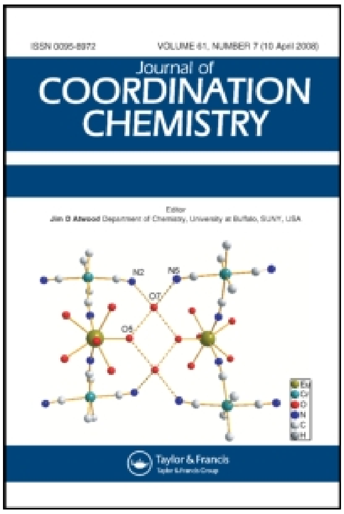

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STRUCTURAL STUDIES OF BRIDGED BIMETALLIC NEODYMIUM AND URANIUM PENTAMETHYLCYCLOPENTADIENYL COMPLEXES: $\{[(C_5Me_5)_2Nd(THF)]_2[\mu\text{-}Cl]\}\{BPh_4\}$ AND $[(C_5Me_5)_2UCl]_2[\mu\text{-}O]$

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The solid state structure of $\{[C_5Me_5)_2Nd(THF)]_2[\mu\text{-}Cl]\}\{BPh_4\}\cdot C_6H_6$, **1**, consists of a cation with THF-solvated decamethylneodymocene units connected symmetrically by a chloride bridge with 2.839(3) Å Nd–(μ-Cl) bonds and a 174.09(10)° Nd–Cl–Nd angle. The $\{BPH_4\}^-$ anion is non-coordinating. The structure of $[(C_5Me_5)_2UCl]_2[\mu\text{-}O]\cdot C_7H_8$, **2**, consists of two chloride ligated $[(C_5Me_5)_2U]$ units bridged symmetrically by a single oxide ion with 2.129(5) Å U–(μ-O) distances and a 167.1(2)° U–O–U angle. Both complexes have normal metrical parameters in the $(C_5Me_5)_2M$ metallocene units.

Keywords: Bimetallic; neodymium; uranium; pentamethylcyclopentadienyl;
X-ray crystallography

INTRODUCTION

The unusual reactivity of $(C_5Me_5)_3Sm$,[1,2] the first *tris*(pentamethylcyclopentadienyl)metal complex, has stimulated interest in the synthesis of other $(C_5Me_5)_3M$ complexes. Since $(C_5Me_5)_3Sm$ was synthesized from the unique divalent samarium precursor, $(C_5Me_5)_2Sm$, alternative synthetic pathways were necessary for other metals. In the course of examining routes to

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$(C_5Me_5)_3Nd$ and $(C_5Me_5)_3U$, two bimetallic uranium and neodymium pentamethylcyclopentadienyl complexes have been isolated in which the metals are connected by a single atom bridge. Although some single-atom bridged bimetallic lanthanide and actinide cyclopentadienyl complexes have been reported previously,[3–8] no example of a cationic single-bridged lanthanide complex has been reported and no example of a simple $[(C_5Me_5)_2UX]_2(\mu\text{-}O)$ complex (X = halide) has been previously characterized. Since these are basic structural types of pentamethylcyclopentadienyl complexes, they should be well defined. Accordingly, their structural features are reported here.

EXPERIMENTAL

X-ray Data Collection, Structure Determination, and Refinement for $\{[(C_5Me_5)_2Nd(THF)]_2[\mu\text{-}Cl]\}\{BPh_4\}\cdot C_6H_6$, 1

Blue cubes of **1** were isolated as a minor product from a green benzene solution of a multi-step synthesis of $[(C_5Me_5)_2Nd][BPh_4]$[9] in which $[NEt_3H][BPh_4]$ was added to $(C_5Me_5)_2Nd(\eta^3\text{-}CH_2CHCH_2)$ prepared from $(C_5Me_5)_2NdCl_2K(THF)_2$[10] and $(CH_2CHCH_2)MgCl$. A small amount of chloride was retained throughout the course of this synthesis. Retention of chloride is not unusual with the electropositive lanthanides which are both oxophilic and halophilic.[11] A blue crystal of approximate dimensions 0.30 × 0.32 × 0.35 mm was mounted on a glass fiber and transferred to a Siemens P4 diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out according to standard procedures.[12] Intensity data were collected at 163 K using a $2\theta/\omega$ scan technique with MoKα radiation. The raw data were processed with a local version of CARESS[13] 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 program.[14] All 10236 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/m with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C^5_{2h}; No.14] is therefore uniquely defined.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Analytical scattering factors for neutral atoms were used throughout the analysis.[15] Hydrogen atoms were included using a riding model. Carbon atoms C(42) and C(43) are disordered. Two components were included for each atom with site-occupancy-factors of 0.50. At convergence $wR2 = 0.1177$ and $GOF = 1.092$ for 775 variables refined against 9779 unique data (as a comparison for refinement on F, $R1 = 0.0536$ for those 6257 data with $F > 4.0\sigma(F)$).

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2UCl]_2[\mu\text{-}O] \cdot C_7H_8$, 2

Dark red crystals of **2** were isolated from a red/brown solution of a reaction of $[(C_5Me_5)_2U(\mu\text{-}Cl)]_3$[16] and $(C_5Me_5)_2Pb$[17] in toluene in which some oxygen contamination occurred. A dark red crystal of approximate dimensions 0.10 × 0.27 × 0.33 mm was mounted on a glass fiber and handled as described above for **1**. All 7274 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/m with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C^5_{2h}; No.14] is therefore uniquely defined.

The structure was solved as described for **1**. There is one toluene molecule present per formula unit. The toluene is represented by two half-molecules, each located about an inversion center and disordered. Atoms C(41), C(43), C(46) and C(49) were assigned site-occupancy-factors of 1.0. The remaining disordered atoms were assigned SOF's of 0.50. Hydrogen atoms associated with the disordered toluene molecules were not included in the refinement. At convergence, $wR2 = 0.0819$ and $GOF = 1.049$ for 446 variables refined against 704 unique data (as a comparison for refinement on F, $R1 = 0.0305$ for those 5697 data with $F > 4.0\sigma(F)$).

RESULTS AND DISCUSSION

$\{[(C_5Me_5)_2Nd(THF)]_2[\mu\text{-}Cl]\}\{BPh_4\} \cdot C_6H_6$, 1

The solid state structure of **1** consists of discrete $\{[(C_5Me_5)_2Nd(THF)]_2[\mu Cl]\}^+$ cations, Figure 1, and $\{BPh_4\}^-$ anions. Although chloride bridged cations of this type have not previously been observed for lanthanides, the complex $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$, **3**, has been crystallographically characterized. Complex **3** contains both a neutral $(C_5Me_5)_2ClSm(\mu\text{-}Cl)SmL(C_5Me_5)_2$, **4**, (L = one oxygen of a tetraglyme) and an anionic

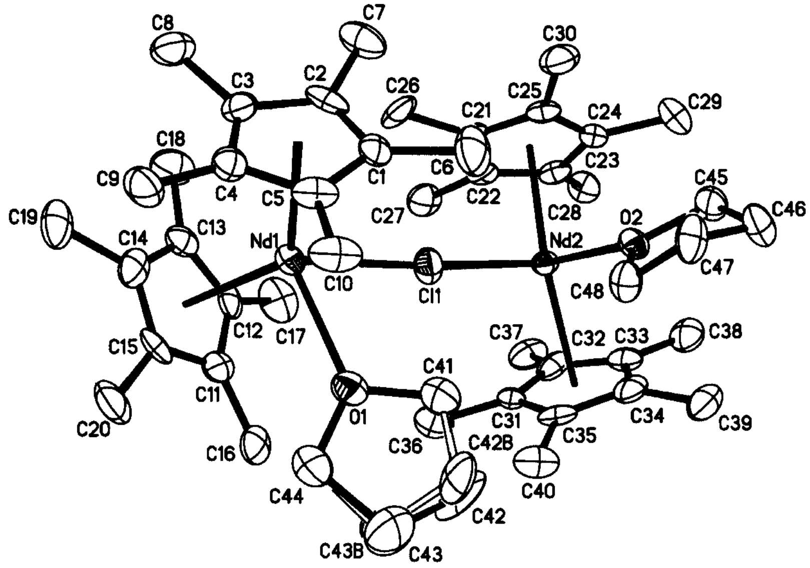

FIGURE 1 Thermal ellipsoid plot of the cation $[(C_5Me_5)_2Nd(THF)]_2[\mu\text{-Cl}]$ of $\{[(C_5Me_5)_2Nd(THF)]_2[\mu\text{-Cl}]\}\{BPh_4\}\cdot C_6H_6$, **1**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms and the cocrystallized benzene molecule have been excluded for clarity.

component, $[(C_5Me_5)_2ClSm]_2(\mu\text{-Cl})^-$, **5**, related to the structure of **1**. Complex **1** shows that these $(C_5Me_5)_2ZLn(\mu\text{-X})LnZ(C_5Me_5)_2$ moieties can also exist as cations (X = halide, *Z* = neutral or anionic ligand).

The neodymium ions in **1** are surrounded by ligands which adopt a coordination geometry common to lanthanide metallocenes: the bent metallocene unit is coordinated to two additional donor atoms to give a formal coordination number of 8.[18] The Nd–C(C_5Me_5) average distance, 2.74(3) Å is equivalent, within error limits, to the 2.72 Å average distances found in both **4** and **5**. The ring centroid–metal-ring centroid angles in **1**, 132.5° and 133.0° are also similar to the 134° average angle in **4** and **5**.

Although the two halves of the cation in **1** are not related by crystallographic symmetry, the two Nd–(μ-Cl) distances, 2.838(3) and 2.841(3) Å, are equivalent within error limits. A similar situation is observed in the anionic complex, **5**, which has chemically equivalent halves and 2.76(1) Å Sm–(μ-Cl) distances. However, the unsymmetrical neutral complex, **4**, has disparate lanthanide–(μ-chloride) distances, 2.89(1) and 2.77(1) Å. The Nd–(μ-Cl) bond lengths in **1** are longer than expected compared to **5** even after considering the difference in Shannon radii which show eight coordinate Nd(III) to be 0.03 Å larger than Sm(III).[19]

Comparison of the Nd–(μ-Cl) distances in **1** with the 2.802(1) and 2.754(2) Å lengths in $\{[Me_2Si(C_5Me_4)]_2NdCl\}_2(\mu\text{-}Cl)Li(THF)_2$[3b] and the 2.841 Å Nd–(μ-Cl) distance in $[Na(C_4H_8O)_6][Nd(\eta^5\text{-}C_9H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]$[3a] is not so straightforward due to the structural differences of these complexes. Not only is the cyclopentadienyl ring substitution different, but the former complex has a cyclic NdClNdClLiCl structure and the latter complex has two *tris*(indenyl) lanthanide units connected by a chloride bridge.

The 174.09(10)° Nd–Cl–Nd angle in **1** is much closer to linear than the analogous 165.1(4) and 164.8(4)° Sm–Cl–Sm angles in **4** and **5**, respectively. Since a linear angle would allow more room around each metal in a sterically crowded complex, this suggests that **1** is more sterically congested than **4** and **5**. This is likely due to the presence of terminal THF ligands in **1** instead of the terminal chloride ligands in **4** and **5**. The longer Nd–(μ-Cl) bond distances in **1** are also consistent with a more crowded environment.

The 2.515(6) Å Nd(1)–O(1) and 2.463(6) Å Nd(2)–O(2) distances in **1** are not equal, but are in the normal range of THF ligands attached to eight-coordinate metallocenes of this type. For example, $(C_5Me_5)_2Nd[O(CH_2)_4C_5Me_5](THF)$[20] has a 2.513(3) Å Nd–O(THF) distance and $(C_5Me_5)_2SmZ(THF)$ complexes have distances ranging from 2.44(2) to 2.577(9) Å.[21]

$[(C_5Me_5)_2UCl]_2[\mu\text{-}O]\cdot C_7H_8$, 2

Crystals of **2** have a structure, Figure 2, related to that of **1** with the general formula $(C_5Me_5)_2ZLn(\mu\text{-}X)LnZ(C_5Me_5)_2$ except that with this tetravalent metal a neutral complex results when Z is chloride and X is an oxide ion. Oxide bridges in $(C_5Me_5)_2U$ complexes have been reported in the literature, but are most commonly found in heteropolymetallic complexes with structures more complicated than that of a simple oxo-bridged dimer.[22,23] To our knowledge, the structures of only three single dimeric oxygen-bridged cyclopentadienyl uranium complexes have been reported: $[\{(C_9H_7)UBr(CH_3CN)_4\}_2(\mu\text{-}O)][UBr_6]$,[4] $[(C_5H_5)_3U]_2[\mu\text{-}O]$,[7a] and $[(Me_3SiC_5H_4)_3U]_2[\mu\text{-}O]$.[7b] A single-atom bridging sulfide complex, $[(MeC_5H_4)_3U]_2(\mu\text{-}S)$ has also been reported.[24] Unfortunately, none of these are bis(cyclopentadienyl) species suitable for direct comparison with **2**.

As in **1**, the two $(C_5Me_5)_2UCl$ halves of **2** are not related by crystallographic symmetry but the 2.131(5) and 2.125(2) Å U–(μ-O) bridging distances are equivalent within error limits. The 2.76(4) Å average U–C(C₅Me₅) bond distance is consistent with the 2.72(2) Å distance found for

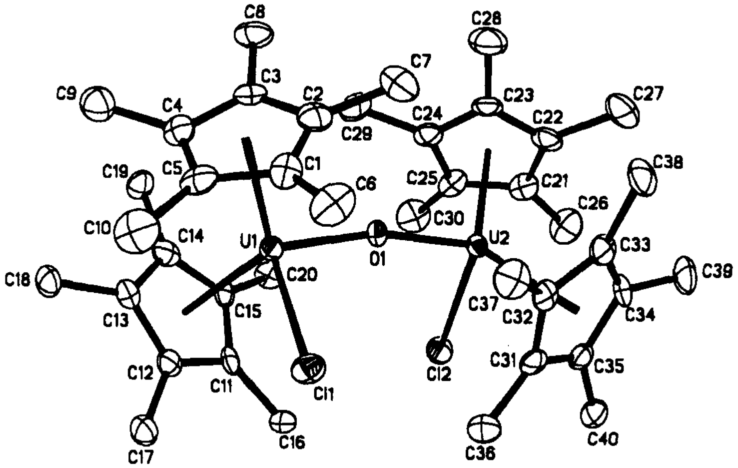

FIGURE 2 Thermal ellipsoid plot of the $[(C_5Me_5)_2UCl]_2[\mu\text{-}O]\bullet C_7H_8$, **2**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms and the cocrystallized toluene molecule have been excluded for clarity.

$(C_5Me_5)_2UCl_2$,[25] as is the 129.3° average (ring centroid)–U-(ring centroid) angle in **2** compared to 132° angle in $(C_5Me_5)_2UCl_2$. The 2.610(2) and 2.6103(15) Å U–Cl bond distances in **2** are also similar to the 2.583(6) Å bond distance in $(C_5Me_5)_2UCl_2$. The U–O–U angle in **2** is 167.1(2)° compared to the 180° angles in $[\{(C_9H_7)UBr(CH_3CN)_4\}_2(\mu\text{-}O)][UBr_6]$,[4] $[(C_5H_5)_3U]_2[\mu\text{-}O]$,[7a] and $[(Me_3SiC_5H_4)_3U]_2[\mu\text{-}O]$,[7b] and a 164.9(4)° U–S–U angle in $[(MeC_5H_4)_3U]_2(\mu\text{-}S)$.[23]

CONCLUSION

The range of structurally characterized, bridged, bimetallic *f*-element $(C_5Me_5)_2ZM(\mu\text{-}X)MZ(C_5Me_5)_2$ complexes has been extended to include cationic lanthanide derivatives, $[(C_5Me_5)_2(THF)Ln(\mu\text{-}X)Ln(THF)(C_5Me_5)_2]^+$ and neutral actinide complexes connected by a single oxide ligand $(C_5Me_5)_2ClU(\mu\text{-}O)UCl(C_5Me_5)_2$.

Supplementary Material

Figures and tables of crystal data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and structure factors are available from W.J.E.

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