cyanide ligands in a similar way. Given the marked differences between Sm(III) and Rh(III), it is unusual to find them in such similar bonding situations.

To our knowledge, complex 2 represents the first crystallographically characterized molecular lanthanide cyanide complex.[29] Although simple lanthanide cyanides have been known since 1972[23] and organometallic lanthanide cyanides such as $(C_5H_5)_2NdCN$ and $(C_5H_5)_2YbCN$ are reported in the literature,[30] no other molecular species have been studied by diffraction techniques.

These samarium-based isocyanide dealkylation reactions (eq 3) also produce organosamarium byproducts which may incorporate the R groups cleaved from the isocyanide ligands. In the cyclohexyl isocyanide system, a byproduct is isolated which has a complete elemental analysis consistent with the formula $(C_5Me_5)_2Sm(C_6H_{11}CNC_6H_{11})$. No evidence for cyclohexane, cyclohexene, or bicyclohexyl was found in the reaction mixture (in contrast to the $(C_5Me_5)_2V/CNC_6H_{11}$ system that forms cyclohexane[44]). An iminoacyl complex such as $(C_5Me_5)_2Sm(C_6H_{11}CNC_6H_{11})$ is a reasonable byproduct of reaction 3 based on the mechanism postulated for the dialkyl phosphorus and trialkyltin reactions (eq 5 and 6) and the isocyanide intermediates isolated in the $(C_5Me_5)_2V$ system. Hence, the isocyanide reagent could displace one or two THF molecules from $(C_5Me_5)_2Sm(THF)_2$ to form $(C_5Me_5)_2Sm(THF)(CNR)$ or $(C_5Me_5)_2Sm(CNR)_2$. Electron transfer would give the radical $(C_5Me_5)_2LSm^{III}\dot{C}{=}NR$ (L = THF or CNR) which could fragment to $(C_5Me_5)_2LSm(CN)$ and R$^\bullet$. A $(C_5Me_5)_2Sm(CNR)(CN)$ complex (analogous to the structurally characterized $(C_5Me_5)_2V(CNR)(CN)$[44]) could trimerize to 2 or 3. R$^\bullet$ could combine with the $(C_5Me_5)_2LSm\dot{C}{=}NR$ intermediate to form $(C_5Me_5)_2Sm(RC{=}NR)$ plus L. Consistent with this, the byproduct of the cyclohexyl isocyanide reaction has an infrared absorption at 1555 cm^{-1} which is in the range observed for early-transition-metal iminoacyl complexes.[48-50] However, definitive identification by X-ray crystallography of the extremely soluble organosamarium byproduct of eq 3 has not yet been accomplished.

Conclusion

$(C_5Me_5)_2Sm(THF)_2$ has been found to promote facile cleavage of the C–N single bond in isocyanides to form the trimeric cyanide complexes $[(C_5Me_5)_2Sm(CNR)(\mu\text{-}CN)]_3$ (R = CMe_3, C_6H_{11}). This reaction demonstrates the potential of $(C_5Me_5)_2Sm(THF)_2$ for selective bond-breaking reactions that require strongly reducing conditions. In addition, this reaction provides an interesting trimeric cyanide-bridged species.

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Registry No. 1, 79372-14-8; 2, 112041-54-0; 2·3C_7H_8, 112041-55-1; 3, 112068-62-9; 3·2THF, 112068-63-0; CNC_6H_{11}, 931-53-3; Me_3CNC, 7188-38-7; $(C_5Me_5)_2SmC_6H_{11}CNC_6H_{11}$, 112021-60-0.

Supplementary Material Available: Tables of complete interatomic distances and angles and thermal parameters (6 pages): a listing of structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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Studies on Rare Earth–Indenyl Compounds. 2. Synthesis and Crystal Structure of Hexakis(tetrahydrofuran)sodium (μ-Chloro)bis(triindenylneodymate)

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By the reaction of lanthanide trichloride with indenylsodium in THF solution the title complex $[Na(C_4H_8O)_6][Nd(\eta^5\text{-}C_9H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]$ was synthesized and characterized by elemental analysis, infrared spectrum, molar conductivity, and X-ray diffraction analysis. The compound crystallized in the triclinic space group $P\bar{1}$ with a = 10.701 (2) Å, b = 12.697 (3) Å, c = 12.838 (2) Å, α = 92.55 (2)°, β = 97.95 (2)°, γ = 88.28 (2)°, and Z = 1. The structure was determined by direct methods and refined by full-matrix least squares to the final R = 0.046 for 6843 observed reflections.

Introduction

Although a series of lanthanide–indenyl compounds, $Ln(C_9H_7)_3{\cdot}THF$, were synthesized and studied by Tsutsui et al. in 1969 (where Ln = La, Sm, Gd, Tb, Dy, Yb)[1] and by Huang et al. in 1985 (where Ln = Ce, Nd, Y),[2] the related crystal structural research has been rather limited.[3]

Here we report the preparation and structural characterization of the first lanthanide–indenyl compound con-

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taining a linear chlorine bridge, $[Na(C_4H_8O)_6][Nd(\eta^5\text{-}C_9H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]$.

Experimental Section

All operations were performed in an atomsphere of prepurified nitrogen by using Schlenk techniques. Solvents were rigorously dried and freshly distilled under nitrogen before use.

Synthesis of $[Na(C_4H_8O)_6][Nd(\eta^5\text{-}C_9H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]$. To a suspension of 2.0 g (7.98 mmol) of $NdCl_3$ in THF at 0 °C was added 12.6 mL of 1.90 N NaC_9H_7 (23.94 mmol). The filtered solution was cooled. Green crystals were isolated by filtration and washed with THF; mp 69 °C dec; Anal. Calcd for $NaNd_2C_{78}H_{90}O_6Cl$ (1470.4): Nd, 19.62; Cl, 2.41; C, 63.71; H, 6.17. Found: Nd, 19.82; Cl, 2.36; C, 63.56; H, 5.86. The molar conductivity of its THF solution (3.14×10^{-3} mol/L) was 17.5 $cm^2/(\Omega \cdot mol)$. IR (KBr, cm^{-1}): 669 m, 691 m, 718 m, 766 m, 826 w, 859 w, 914 w, 942 w, 1019 w, 1067 w, 1392 s, 1419 s, 1632 w, 2854 m, 2925 m, 2957 m, 3070 m. MS (20 eV): *m/z* (relative intensity) 72 (26.18, THF), 115 (100, C_9H_7), 489 (0.52, $Nd(C_9H_7)_3$).

Crystal Structure Analysis. A crystal of dimensions 0.15 × 0.2 × 0.4 mm^3 was chosen and sealed into a capillary under N_2 atmosphere. The unit cell parameters were refined from the setting angles of 25 reflections measured on an Enraf-Nonius CAD-4 diffractometer. Intensities of 8038 reflections with $\theta \leqslant 28°$ were collected by using graphite-monochromated Mo K_α radiation $\lambda = 0.71073$ Å) and ω -2θ scanning mode at 20 °C, 6843 of which were considered observed ($I \geqslant 3\sigma(I)$) after Lorentz and polarization and empirical absorption corrections. The Enraf-Nonius Structure Determination Package (SDP-PLUS) was used for all data reduction and structure refinement. As the output intensity statistics and the zero-moment test tended toward a noncentrosymmetric space group, the determination was performed in the space group *P*1 first. The structure was solved by Multan 11/82 which revealed the positions of the two neodymium atoms. A series Fourier syntheses afforded the location of the remaining atoms. After several cycles of refinements, it was clear that the two halves of the anion and the cation were related by a center of symmetry. The space group was thus changed to $P\bar{1}$, which required the postulation of disorder for the third indenyl ring bonded to the metal atom and for some atoms of the THF molecules. The non-hydrogen atoms except the disordered ones were refined anisotropically. Those exhibiting disorder were refined with isotropic thermal parameters after the occupancy factors had converged. Full-matrix least-squares refinement was carried out by using unit weights for all 6843 reflections for which $I \geq 3\sigma(I)$. The refinement included an extinction correction and converged to $R = 0.046$. No attempt was made to locate any of the hydrogen atoms. The final difference electron density map shows there is no peak higher than 0.9 e/Å^3. Neutral atomic scattering factors were used from the literature.[4] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[4]

Final positional parameters are given in Table I. Bond lengths and angles are listed in Tables II and III. Views of the anion are shown in Figure 1.

Results and Discussion

The title compound consists of an ion pair: the cation $[Na(C_4H_8O)_6]^+$ and the anion $[Nd(\eta^5\text{-}C_9H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]^-$. The molar conductivity in THF solution (3.14×10^{-3} mol/L), 17.5 $cm^2/(\Omega \cdot mol)$, is comparable with that of the ionic compound $[Li(TMEDA)_2][Yb(CH_2SiMe_3)_4]$, 21.2 $cm^2/(\Omega \cdot mol)$,[5] and is consistent with an ionic formulation.

The crystal structure is very similar to that of the compound $[Na(C_4H_8O)_6][Cp_3Lu(\mu\text{-}H)LuCp_3]$.[6] In either

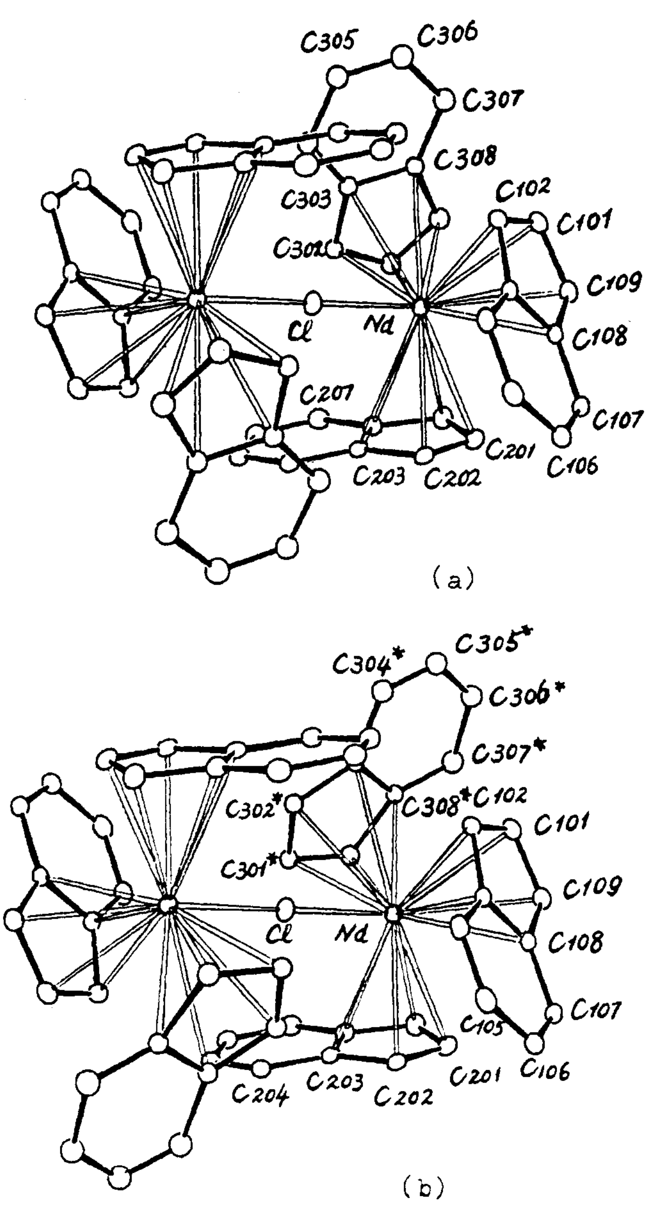

Figure 1. Views of the anion $[Nd(\eta^5\text{-}C_9H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]$, either a or b with one set of probable arrangements of the third indenyl ring.

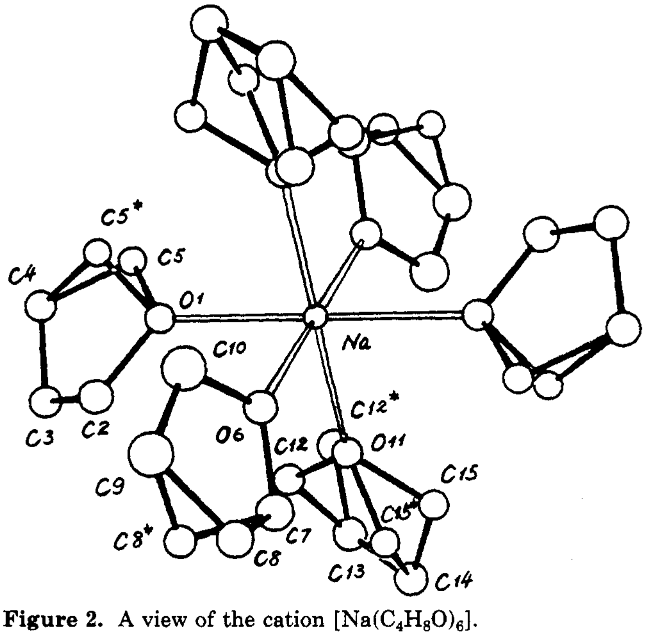

Figure 2. A view of the cation $[Na(C_4H_8O)_6]$.

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Table I. Positional Parameters and Their Estimated Standard Deviations (Esd's) in Parentheses

atom	x	y	z	B (eq), Å^2	mult
Cl	0.500	0.500	0.500	5.92 (5)	1.000
Nd	0.37409 (3)	0.34757 (2)	0.59880 (2)	3.900 (5)	1.000
C101	0.4849 (6)	0.3029 (5)	0.7990 (5)	5.6 (1)	1.000
C102	0.5695 (6)	0.3691 (5)	0.7581 (4)	5.2 (1)	1.000
C103	0.6336 (5)	0.3035 (4)	0.6866 (4)	4.2 (1)	1.000
C104	0.7330 (6)	0.3234 (5)	0.6285 (5)	5.2 (1)	1.000
C105	0.7823 (6)	0.2407 (6)	0.5729 (5)	5.8 (2)	1.000
C106	0.7343 (6)	0.1366 (5)	0.5709 (5)	5.4 (1)	1.000
C107	0.6346 (6)	0.1160 (5)	0.6245 (4)	4.8 (1)	1.000
C108	0.5833 (5)	0.2002 (4)	0.6830 (4)	4.2 (1)	1.000
C109	0.4859 (6)	0.2019 (5)	0.7496 (5)	5.2 (1)	1.000
C201	0.3493 (6)	0.1523 (5)	0.4993 (5)	5.6 (1)	1.000
C202	0.4099 (6)	0.2121 (4)	0.4333 (5)	4.8 (1)	1.000
C203	0.3156 (5)	0.2814 (4)	0.3794 (4)	4.2 (1)	1.000
C204	0.3194 (6)	0.3539 (5)	0.2996 (5)	4.9 (1)	1.000
C205	0.2081 (6)	0.4045 (5)	0.2579 (5)	5.3 (1)	1.000
C206	0.0930 (6)	0.3873 (5)	0.2959 (5)	5.5 (1)	1.000
C207	0.0863 (6)	0.3196 (5)	0.3747 (5)	5.6 (1)	1.000
C208	0.1985 (5)	0.2640 (4)	0.4183 (5)	4.8 (1)	1.000
C209	0.2211 (7)	0.1863 (5)	0.4962 (6)	6.0 (2)	1.000
C301	0.123 (1)	0.3858 (8)	0.6307 (8)	5.8 (2)**	0.641
C302	0.1658 (8)	0.4780 (7)	0.5904 (7)	4.3 (2)**	0.641
C303	0.2421 (8)	0.5319 (7)	0.6750 (7)	4.5 (2)**	0.641
C304	0.303 (1)	0.6301 (8)	0.6834 (8)	5.5 (2)**	0.641
C305	0.363 (1)	0.6624 (9)	0.7824 (9)	6.0 (2)**	0.641
C306	0.371 (1)	0.605 (1)	0.867 (1)	6.9 (3)**	0.641
C307	0.312 (1)	0.5052 (9)	0.8646 (9)	6.2 (2)**	0.641
C308	0.2474 (9)	0.4696 (7)	0.7637 (7)	4.6 (2)**	0.641
C309	0.175 (1)	0.3760 (9)	0.7308 (9)	6.0 (2)**	0.641
C301*	0.183 (1)	0.499 (1)	0.568 (1)	4.3 (3)**	0.359
C302*	0.273 (1)	0.558 (1)	0.634 (1)	4.4 (3)**	0.359
C303*	0.291 (1)	0.525 (1)	0.740 (1)	4.3 (3)**	0.359
C304*	0.360 (2)	0.568 (2)	0.842 (2)	6.1 (4)**	0.359
C305*	0.355 (2)	0.528 (2)	0.927 (2)	6.2 (4)**	0.359
C306*	0.283 (2)	0.443 (2)	0.931 (2)	6.1 (4)**	0.359
C307*	0.208 (2)	0.393 (2)	0.843 (2)	6.5 (4)**	0.359
C308*	0.215 (1)	0.435 (1)	0.747 (1)	4.1 (3)**	0.359
C309*	0.142 (2)	0.421 (1)	0.634 (1)	5.1 (3)**	0.359
Na	0.0000	0.0000	0.0000	4.54 (6)	1.000
O1	−0.0747 (5)	0.1782 (4)	−0.0254 (4)	6.9 (1)**	1.000
C2	−0.0708 (9)	0.2558 (8)	0.0645 (8)	9.2 (2)**	1.000
C3	0.0427 (9)	0.3591 (7)	0.0163 (7)	8.2 (2)**	1.000
C4	−0.1096 (8)	0.3470 (7)	−0.0950 (7)	8.0 (2)**	1.000
C5	−0.091 (1)	0.228 (1)	−0.130 (1)	6.3 (2)**	0.595
C5*	−0.158 (2)	0.231 (1)	−0.102 (1)	5.9 (3)**	0.405
O6	−0.0639 (5)	0.0140 (4)	0.1705 (4)	7.9 (1)**	1.000
C7	0.018 (1)	0.0283 (8)	0.2694 (8)	9.7 (3)**	1.000
C8	−0.062 (1)	0.020 (1)	0.351 (1)	8.6 (3)**	0.652
C8*	−0.083 (2)	0.079 (2)	0.346 (2)	6.5 (5)**	0.348
C9	−0.197 (1)	0.054 (1)	0.298 (1)	12.9 (4)**	1.000
C10	−0.198 (1)	0.031 (1)	0.187 (1)	13.3 (4)**	1.000
O11	0.2090 (5)	0.0661 (4)	0.0638 (4)	7.3 (1)**	1.000
C12	0.246 (1)	0.172 (1)	0.047 (1)	8.0 (3)**	0.720
C12*	0.282 (3)	0.135 (3)	−0.014 (3)	9.6 (9)**	0.280
C13	0.390 (1)	0.1634 (8)	0.0585 (8)	9.7 (3)**	1.000
C14	0.4181 (9)	0.0811 (8)	0.1412 (8)	9.3 (2)**	1.000
C15	0.314 (1)	−0.002 (1)	0.111 (1)	7.1 (3)**	0.560
C15*	0.293 (2)	0.049 (1)	0.162 (1)	6.7 (4)**	0.440

[a] Parameters with a double asterisk were refined isotropically. Anisotroically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)\ [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table II. Selected Bond Lengths (Å) and Angles (deg) in the Anion $[Nd(C_9H_7)_3(\mu\text{-}Cl)Nd(C_9H_7)_3]^-$ with Their Esd's in Parentheses

	Bond Lengths		
Nd–C101	2.753 (5)	Nd–C301	2.796 (11)
Nd–C102	2.726 (4)	Nd–C302	2.730 (9)
Nd–C103	2.896 (4)	Nd–C303	2.900 (7)
Nd–C108	2.990 (4)	Nd–C308	3.016 (8)
Nd–C109	2.854 (5)	Nd–C309	2.901 (9)
Nd–C201	2.741 (5)	Nd–C301*	2.769 (15)
Nd–C202	2.735 (4)	Nd–C302*	2.892 (13)
Nd–C203	2.892 (4)	Nd–C303*	3.019 (12)
Nd–C208	2.953 (4)	Nd–C308*	2.889 (14)
Nd–C209	2.824 (5)	Nd–C309*	2.71 (2)
Nd–Cp(1)	2.57 (2)	Nd–Cl	2.841
Nd–Cp(2)	2.56 (3)	Nd–Cp(av)	2.58
Nd–Cp(3)	2.61 (3)	Cp(3)-Cp(3*)	0.65 (4)
Nd–Cp(3*)	2.58 (5)		
C101–C102	1.420 (8)	C201–C202	1.398 (7)
C101–C109	1.406 (7)	C201–C209	1.421 (8)
C102–C103	1.442 (6)	C202–C203	1.441 (6)
C103–C104	1.415 (7)	C203–C204	1.413 (6)
C104–C105	1.377 (7)	C204–C205	1.388 (7)
C103–C108	1.429 (6)	C203–C208	1.438 (6)
C105–C106	1.430 (8)	C205–C206	1.412 (8)
C106–C107	1.383 (7)	C206–C207	1.367 (7)
C107–C108	1.421 (6)	C207–C208	1.432 (7)
C108–C109	1.436 (7)	C208–C209	1.428 (7)
Ring 3		Ring 3*	
C301–C302	1.41 (1)	C301*–C302*	1.40 (2)
C301–C309	1.34 (1)	C301*–C309*	1.45 (2)
C302–C303	1.43 (1)	C302*–C303*	1.43 (2)
C303–C304	1.42 (1)	C303*–C304*	1.51 (2)
C304–C305	1.39 (1)	C304*–C305*	1.23 (3)
C303–C308	1.41 (1)	C303*–C308*	1.43 (2)
C305–C306	1.33 (1)	C305*–C306*	1.35 (2)
C306–C307	1.43 (2)	C306*–C307*	1.44 (2)
C307–C308	1.44 (1)	C307*–C308*	1.38 (2)
C308–C309	1.45 (1)	C308*–C309*	1.56 (2)
	Bond Angles		
C102–C101–C109	110.4 (5)	C202–C201–C209	110.3 (5)
C101–C102–C103	106.4 (4)	C201–C202–C203	107.2 (4)
C102–C103–C104	132.2 (5)	C202–C203–C204	132.7 (5)
C102–C103–C108	107.9 (4)	C202–C203–C208	107.5 (4)
C104–C103–C108	119.8 (4)	C204–C203–C208	119.8 (4)
C103–C104–C105	118.6 (5)	C203–C204–C205	118.9 (5)
C104–C105–C106	121.8 (5)	C204–C205–C206	121.3 (5)
C105–C106–C107	120.6 (5)	C205–C206–C207	121.5 (5)
C106–C107–C108	118.3 (5)	C206–C207–C208	119.0 (5)
C103–C108–C107	120.8 (4)	C203–C208–C207	119.6 (5)
C103–C108–C109	108.2 (4)	C203–C208–C209	108.1 (4)
C107–C108–C109	130.9 (5)	C207–C208–C209	132.3 (5)
C101–C109–C108	106.8 (5)	C201–C209–C208	106.7 (5)
C302–C301–C309	110 (1)	C302*–C301*–C309*	105 (1)
C301–C302–C303	107.3 (9)	C301*–C302*–C303*	113 (1)
C302–C303–C304	132.8 (8)	C302*–C303*–C304*	134 (1)
C302–C303–C308	107.0 (8)	C302*–C303*–C308*	110 (1)
C304–C303–C308	120.2 (8)	C304*–C303*–C308*	116 (1)
C303–C304–C305	117.2 (8)	C303*–C304*–C305*	123 (2)
C304–C305–C306	123.7 (9)	C304*–C305*–C306*	120 (2)
C305–C306–C307	122 (1)	C305*–C306*–C307*	125 (2)
C306–C307–C308	116 (1)	C306*–C307*–C308*	115 (2)
C303–C308–C307	120.9 (9)	C303*–C308*–C307*	121 (2)
C303–C308–C309	107.1 (8)	C303*–C308*–C309*	103 (1)
C307–C308–C309	131.9 (8)	C307*–C308*–C309*	136 (2)
C301–C309–C308	108.2 (9)	C301*–C309*–C308*	109 (1)
Cp(1)–Nd–Cp(2)	115.2 (5)	Cp(2)–Nd–Cp(3*)	120.4 (7)
Cp(1)–Nd–Cp(3)	114.9 (6)	Cp(2)–Nd–Cl	102.3 (2)
Cp(1)–Nd–Cp(3*)	117.4 (7)	Cp(3)–Nd–Cl	106.3 (4)
Cp(1)–Nd–Cl	102.4 (2)	Cp(3)–Nd–Cp(3*)	14.4 (8)
Cp(2)–Nd–Cp(3)	113.7 (6)	Cp(3*)–Nd–Cl	92.1 (5)

structure the coordination number of the lanthanoid atom is ten. Both compounds are ionic and have as the cation $[Na(C_4H_8O)_6]^+$, and the anions are similar. Both cation and anion have inversion centers where the Na^+ and H^- or Cl^- ions are located. The distance from Cl^- to Na^+ in the compound is about 10 Å.

In the anion $[Nd(\eta^5\text{-}C_9H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]^-$, two Nd atoms are bonded by a bridging Cl^- ion at a distance of Nd–Cl = 2.831 Å and respectively η^5- bonded to the carbon atoms of five-membered ring of each of three indenyl groups at distances of 2.71 (2)–3.02 (1) Å. Of these three indenyl rings, one is disordered and may have two sets of probable positions around the lanthanoid atom with corresponding occupancies of 0.641 and 0.359. Figure 1 presents views of the anion, either a or b with one set of the probable positions for the disordered indenyl ring. It

Table III. Bond Lengths (Å) and Angles (deg) in the Cation $[Na(C_4H_8O)_6]^+$ with Their Esd's in Parentheses

	Bond Lengths		
Na–O1	2.397 (4)	C7–C8*	1.65 (2)
Na–O6	2.380 (5)	C8–C9	1.57 (2)
Na–O11	2.434 (4)	C9–C8*	1.33 (2)
O1–C2	1.481 (8)	C9–C10	1.445 (13)
O1–C5	1.501 (11)	O11–C12	1.453 (11)
O1–C5*	1.417 (14)	O11–C12*	1.64 (3)
C2–C3	1.530 (10)	O11–C15	1.479 (12)
C3–C4	1.511 (9)	O11–C15*	1.460 (14)
C4–C5	1.574 (12)	C12–C13	1.532 (13)
C4–C5*	1.566 (15)	C13–C12*	1.42 (3)
O6–C7	1.446 (9)	C13–C14	1.517 (10)
O6–C10	1.489 (11)	C14–C15	1.553 (14)
C7–C8	1.455 (14)	C14–C15*	1.47 (2)
	Bond Angles		
O1–Na–O6	88.2 (2)	O1–Na–O6′	91.8 (2)
O1–Na–O11	89.1 (1)	O1–Na–O11′	90.9 (1)
O6–Na–O11	92.8 (2)	O6–Na–O11′	87.2 (2)
C2–O1–C5	113.4 (6)	C7–O6–C10	110.2 (7)
C2-O1–C5*	100.5 (7)	O6–C7–C8	106.1 (8)
O1–C2–C3	103.2 (6)	O6–C7–C8*	101.0 (9)
C2–C3–C4	102.9 (6)	C7–C8–C9	104 (1)
C3–C4–C5	106.4 (6)	C7–C8*–C9	106 (1)
C3–C4–C5*	103.7 (7)	C8–C9–C10	106 (1)
O1–C5–C4	100.2 (7)	C10–C9–C8*	112 (1)
O1–C5*–C4	104.4 (9)	O6–C10–C9	106.1 (9)
C12–O11–C15	113.7 (7)	C15–O11–C12*	100 (1)
C12*–O11–C15*	109 (1)	C12–O11–C15*	98.1 (8)
O11–C12–C13	103.4 (7)	O11–C12*–C13	99 (2)
C12–C13–C14	101.6 (7)	C14–C13–C12*	110 (1)
C13–C14–C15	104.8 (7)	C13–C14–C15*	104.7 (8)
O11–C15–C14	100.3 (8)	O11–C15*–C14	105 (1)

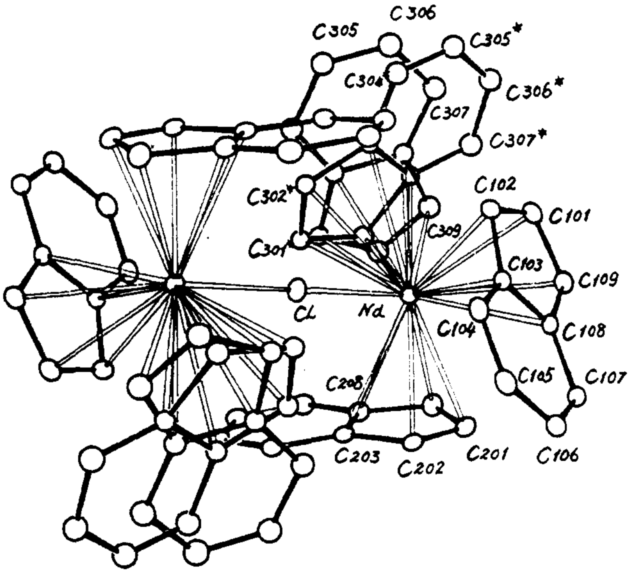

Figure 3. A view of the anion $[(C_9H_7)_3Nd(\mu\text{-}Cl)Nd(C_9H_7)_3]$.

is clear from the Figure and Table II that the two five-membered rings of these disordered indenyl groups are very near one another (center-to-center distance = 0.65 Å), but the six-membered rings are oriented quite differently. From the distance Nd–Cl approximating to the separation of Cl^- (1.81 Å)–Nd^{3+} (1.11 Å)[7] and the linear link Nd–Cl–Nd, the bond Nd–Cl is principally ionic in nature. For Nd^{3+} with coordination number ten, the ionic radius[7] is 1.20 Å, leading to a derived radius for chloride of 1.63 Å. This value is within the range 1.61–1.76 Å for the bridging chloride in a series of cyclopentadienyl homometallic bridged dimers.[8,9] Since the ionic radius of Nd^{3+} is about 0.14 Å longer than that of Lu^{3+}, the average carbon–neodymium bond length, 2.849 Å, is comparable with the 2.71-Å Lu–C(Cp) bond in compound $[Na(C_4H_8O)_6][LuCp_3(\mu\text{-}H)LuCp_3]$. The value is also in good agreement with the 2.703–2.895 Å value in $Nd(CH_3C_5H_4)_3$[10] and the 2.81–2.94 Å value in $[Nd_2O(C_5H_5)_6][(C_{12}H_9N_2)_3Cl\cdot mC_4H_8O]$[11] and is also comparable with the 2.75-Å average samarium–carbon separation in $Sm(\eta^5\text{-}C_9H_7)_3$.[3]

The nine-carbon indenyl ring systems are approximately planar with very small dihedral angles between the five- and six-membered-ring planes (5.0, 3.9, 3.7, and 6.3° for the indenyl groups 1, 2, 3, and 3*, respectively; groups 3 and 3* are of two sets of positions for the disordered indenyl). Although these five-membered rings are η^5- bonded to the Nd atom, some significant lengthening of bonds from carbon atoms in the 8,9-positions to the neodymium atom is found, which may result from the steric interference of the benzene rings. The distances from neodymium to the centers of five-membered rings which lie at three corners of a distorted tetrahedron (the centers of indenyl rings 1, 2, 3, and 3*, are abbreviated to Cp(1), Cp(2), Cp(3), and Cp(3*) in Table II) are 2.57 (2), 2.56 (3), 2.61 (3), and 2.58 (5) Å, respectively, and the angle values from Nd^{3+} to two nearby corners including the chloride ion are 92.1 (5)–120.4 (7)°. These values are also comparable with those in compound $[Na(C_4H_8O)_6][LuCp_3(\mu\text{-}H)LuCp_3]$, 2.408 (11)–2.45 (2) Å and 99.6–121.6(6)°; it is reasonable that steric interference of the indenyl ring is greater than that of the cyclopentadienyl ring. As for the disordered ligand, such as the disordered indenyl ring in this compound, observed in organolanthanides with high coordination number recently,[6,12] it may result from the packing in the crystal or from something else. In the indenyl rings most of bond lengths and angles (given in Table II) are within the range expected for five- and six-membered conjugated ring systems, but a few have significant deviations. Similar variations have been observed in virtually all the reported cyclopentadienyl and indenyl structures[3,13] and probably result from systematic errors in the data and from some degree of disorder of the third indenyl ring as well.

In the cation $[Na(C_4H_8O)_6]^+$, the sodium ion is solvated and octahedrally bonded to the oxygen atoms of six THF molecules. Thus the solvated cation is compatible with the anion in size (radii about 4.70 and 5.50 Å, respectively). This makes the system more stable, perhaps, that is why the crystal structure exists in the form of isolated ions rather than of tetrameric[10] or polymeric[14] lanthanide compounds. The bond lengths Na–O, 2.380 (5)–2.434 (4) Å, and angles for two nearby oxygen atoms to the sodium, 88.2 (2)–92.8 (2)°, are a little different from the 2.340 (10)–2.441 (10) Å and 88.8 (4)–91.2 (4)° values in compound $[Na(C_4H_8O)_6][LuCp_3(\mu\text{-}H)LuCp_3]$. Due to the high degree of disorder, the bond lengths and angles of solvent molecules within the cation shown in Table III are rather deviated from normal values. This is common for all the THF-solvated compounds.

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Registry No. $[Na(C_4H_8O)_6][Nd(\eta^5\text{-}C_4H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]$, 112630-30-5; $NdCl_3$, 10024-93-8; NaC_6H_7, 23181-84-2.

Supplementary Material Available: Tables of crystal data, general temperature factor expressions, positional parameters, bond distances, bond angles, and least squares planes (10 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

Redox Chemistry of the Cluster $[Os_{10}C(CO)_{24}]^{2-}$

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The dianion $[Os_{10}C(CO)_{24}]^{2-}$ (1) is oxidized at a hanging drop mercury electrode (HDME) in a variety of media to produce $[Os_{20}(C)_2(CO)_{48}Hg_2]^{2-}$ (2), which on standing ultimately yields the known $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (3). The dianion 1 is readily reduced electrochemically (at wave A in the cyclic voltammogram) by two electrons to yield the tetraanion $[Os_{10}C(CO)_{24}]^{4-}$ (5). This reduction was studied at a variety of electrodes and in different media and was found to be associated with an oxidation at more positive potentials (wave C). Electrochemical studies of 5 showed that 1 and 5 could be readily interconverted in close to 100% yield showing that the two redox processes were chemically reversible. From a comparison of the electrochemical and IR properties of 1 and 5 it was concluded that the two-electron reduction of 1 generated 5 with an associated minor change in structure, a process that was reversed upon oxidizing at wave C. When a solution of 1 is cooled, the two-electron wave (wave A) split into a quasi-reversible one-electron process and an irreversible wave which moved to more negative potentials as the temperature was reduced. The broad wave was linked to the oxidative feature (wave C) and demonstrated that the structural change occurs on the addition of the second electron to 1. The quasi-reversible electrochemical process was associated with the formation of the trianion $[Os_{10}C(CO)_{24}]^{3-}$ (4) which could be independently synthesized by the slow chemical reduction of 1. As suggested by the electrochemical results, samples of 4 disproportionated at room temperature and hence could not be further characterized. The species 2–5 have been prepared by independent chemical methods.

Introduction

Oxidized and reduced states of large metal carbonyl clusters are of increasing interest. This is due in part to their higher reactivity and also to the possible analogy between the binding of ligands to a metal cluster and the binding of ligands to a metal surface.[1,2] The chemistry and reactivity of high nuclearity osmium clusters has been previously reported,[3] but little information on the redox chemistry of these species and the related high nuclearity nickel, cobalt, and rhodium species is available.[4] However, of the larger clusters that have been studied by electrochemical techniques it has been reported that the addition or removal of electrons is often associated with changes in structure. Well-defined examples include $[FeCpS]_4$ and $[FeCp(CO)]_4$ which both show several reversible one-electron steps, each associated with a small change in the structure of the cluster.[5,6] In a similar way $[Au_9(PPh_3)_8]^{3+}$ shows two reversible one-electron processes and a structural change,[7] but in all these cases the electrochemically reversible nature of the waves in the cyclic voltammogram (CV) show that the structural changes are fast and reversible.[8] With osmium carbonyl clusters evidence is mounting[9,10] that the stronger Os–Os bonds lead to higher activation energies for structural changes generating electrochemically irreversible features in the CV. The reductive electrochemistry of 1 shows two linked irreversible electrochemical waves. Such features are usually associated with slow electron-transfer caused by a change in structure of the cluster. Further studies showed that the two-electron reduction of 1 could be split into two one-electron processes. The addition of the first electron was found to be fast and electrochemically reversible, but the addition of the second electron is slower and appeared to be associated with the expected change in cluster structure. Evidence that the structural change in a cluster occurred upon the addition of the second electron has been previously reported,[7] but this is the first time that the

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