Synthesis, Characterization, and Solid-State Structural Determination of Tris(2,4-dimethylpentadienyl)neodymium, $Nd(2,4-C_7H_{11})_3$

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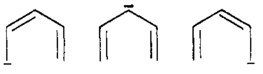
The highly ionic compound $Nd(2,4-C_7H_{11})_3$ has been synthesized and characterized by elemental analysis, infrared, NMR, and electronic spectroscopy, magnetic susceptibility, and a single-crystal X-ray diffraction study ($R = 0.088$, $R_w = 0.125$). The space group is C_i^1—$P\bar{1}$ (No. 2), with unit cell parameters $a = 12.793$ (7) Å, $b = 13.012$ (4) Å, $c = 8.419$ (5) Å, $\alpha = 91.42$ (4)°, $\beta = 107.29$ (4)° and $\gamma = 118.90$ (4)°. The complex possesses idealized C_{3h} symmetry with average Nd–C(1,5), Nd–C(2,4), and Nd–C(3) bond distances of 2.801 (9), 2.855 (8), and 2.749 (10) Å, respectively. These distances reflect the expected relative charge densities for the various carbon atoms and indicate predominately ionic bonding. The 2,4-dimethylpentadienyl ligands are nearly planar, with the carbon atoms in the 2- and 4-positions bent out of the plane in a direction away from the Nd(III) ion, and the carbon atoms in the 1-, 3-, and 5-positions bent in a direction toward the Nd(III) ion. Two different sets of delocalized C–C bond distances are observed, averaging 1.373 (12) and 1.421 (12) A, attributable to a resonance hybrid in which negative charge is localized on the carbon atom in the 3-position. The bonding within the complex is discussed and compared to other organolanthanide and organoactinide structures.

Introduction

The chemistry of the lanthanide metals is generally dominated by the highly ionic trivalent oxidation state.[1] Indeed, even organometallic compounds of the trivalent lanthanide(III) ions are nearly completely ionic, as was readily surmised in the early studies on the $Ln(C_5H_5)_3$, $Ln(C_8H_8)_2^-$, and $[Ln(C_8H_8)Cl(THF)_2]_2$ (Ln = lanthanide metal ion) compounds,[2-4] as well as in the many studies which have followed. Perhaps most notable of the attempts to bring about more unusual bonding patterns in organolanthanide chemistry have been the metal atom studies of Evans and co-workers involving the cocondensation of lanthanide metals with unsaturated organic substrates such as butadienes or acetylenes.[5] Unfortunately, however, no structural data have yet appeared concerning these unusual compounds, which do not seem to involve trivalent lanthanide ions.

One possible means by which one could gauge the extent of interaction between a trivalent lanthanide ion and a formally neutral carbon atom would be to employ a pentadienyl anion as a ligand. Such an anion exists in three resonance forms as indicated below (Ia–c) in which the



Ia Ib Ic

anionic charge is localized in the 1-, 3-, and 5-positions, leaving the 2,4-positions uncharged. Since the 3-position is known to possess more anionic character than the 1,5-positions[6] it might be expected that in some circumstances a lanthanide(III) metal ion could engage in bonding interactions between all three charged carbon atoms of a planar pentadienyl ligand and hence also be brought into the proximity of the uncharged carbon atoms at positions 2 and 4, thereby allowing for the first time a close structural examination of the interaction between a trivalent lanthanide ion and a neutral carbon atom. Above and beyond this consideration, the synthetic and structural results presented herein could also be of some bearing on the anionically induced polymerization of olefins or polyenes, as well as serving to introduce a more versatile ligand (by reason of possible η^5–η^3–η^1 or other isomerizations) into the field of organolanthanide chemistry. We report herein our observations on the chemical and structural nature of tris(2,4-dimethylpentadienyl)neodymium.

Experimental Section

All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus or in a glovebox. Nonaqueous solvents were throughly dried and deoxygenated in a manner appropriate to each and were distilled under nitrogen immediately prior to use. Carbon and hydrogen analyses were obtained from Bernhardt Laboratories. Neodymium was analyzed by an indirect EDTA titration.[4] Commerically anhydrous neodymium trichloride was freed of final traces of water by reflux with thionyl chloride. 2,4-Dimethyl-1,3-pentadiene was obtained from Chemical Samples Co., and converted to the potassium salt of the 2,4-dimethylpentadienyl anion by a reported procedure.[7]

Spectroscopic Studies. Infrared spectra were recorded on a Perkin-Elmer Model 298 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. All infrared spectra were calibrated with polystyrene. Proton NMR spectra were obtained with Varian FT-80 and SC-300 spectrophotometers using C_6D_6 as solvent and C_6D_5H as internal standard. Electronic spectra were recorded on a Cary-14 spectrophotometer. Solutions were prepared from weighed samples in Schlenk apparatus by the addition of known volumes of solvent (THF) under a nitrogen atmosphere, after which they were transferred to one of a set of matched quartz cells under nitrogen. A conservative estimate of the error in reported extinction coefficients is ±10%. Magnetic susceptibility measurements were obtained by the Evans method,[8] and corrected for diamagnetism.

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Tris(2,4-dimethylpentadienyl)neodymium, Nd(2,4-C_7H_{11})$_2$. To a magnetically stirred slurry of 2.00 g (7.98 mmol) of anhydrous neodymium trichloride in 20 mL THF (THF = tetrahydrofuran) under nitrogen at −78 °C was added dropwise a solution of 3.22 g (23.98 mmol) of $K^+(2,4\text{-}C_7H_{11}^-)$ in ca. 30 mL of THF. After the addition was completed, the mixture was allowed to slowly warm to room temperature, by which time a bright, fluorescent green solution was obtained. After being stirred for an additional 24 h, the solution was filtered from remaining metal chlorides and the solvent was removed in vacuo. The product was then extracted into 50 mL of a 5% THF solution in toluene. After a second filtration, the solvent was removed in vacuo and the compound was isolated by recrystallization from a saturated THF or diethyl ether solution by cooling to −78 °C, leading to a bright green (red by transmittance) crystalline or microcrystalline product. The product so obtained is highly sensitive to air and water and is soluble in most organic solvents.

Anal. Calcd for $C_{21}H_{33}Nd$: C, 58.69; H, 7.74; Nd, 33.56. Found: C, 55.56; H, 7.36; Nd, 33.20.

Complete infrared data (Nujol mull): 3061 (m), 1579 (w, sh), 1560 (m), 1546 (m) 1530 (br, sh), 1508 (w, sh), 1488 (m,sh), 1269 (m), 1226 (w), 1068 (mw), 1038 (mw), 1027 (mw), 989 (w), 888 (w), 814 (ms), 770 (s), 692 (m), 647 (m) cm^{-1}.

^1H NMR (C_6H_6): δ 20.6 (2 H), 8.5 (1 H), −1.7 (6 H), −29.8 (2 H).

X-ray Diffraction Study of Tris(2,4-dimethylpentadienyl)neodymium. Relatively well-formed single crystals could be obtained by slow cooling (1–2 days) of a concentrated solution of the compound in ether to −78 °C. These crystals unfortunately contained solvent ether in the lattice, and as a result the crystals very rapidly deteriorated when removed from the supernatant. Attempts were made to crystallize this compound (or an orange holmium analogue) from less volatile solvents; however, the crystals obtained either possessed very large unit cells or were twinned. Therefore, the ether-containing crystals were chosen for data collection. Many attempts to load these crystals failed due to the loss of ether from the lattice. Eventually, several crystals were loaded successfully by bubbling prepurified nitrogen through diethyl ether prior to its reaching the Schlenk tubes containing the single crystals and the capillaries. The crystals were then sealed under the ether saturated atmosphere in glass capillaries. It was found that rather large crystals had to be employed to reduce solvent loss to an acceptable level. The few crystals so loaded tended to have an effective lifetime of ca. 3 weeks. Because of the relatively short lifetimes of these crystals, standard $P\bar{1}$ software programs were used to determine the unit cell data. In each case, a primitive triclinic unit cell could be chosen with a volume close to that expected for two molecules of the compound. A careful examination of the reduced unit cell parameters indicated that this cell was nearly related to a larger orthorhombic cell, or to three corresponding monoclinic cells. However, in each case, and for each crystal, the unit cell angles were far enough from 90° (a minimum of 10–15 standard deviations) to allow the conclusion that the unit cell was really triclinic. Accurate cell constants and their standard deviations were derived from a least-squares refinement of 15 centered reflections for which $25° < 2\theta < 35°$, using the Mo K$\bar{\alpha}$ peak at 0.710 730 Å. The unit cell parameters are a = 8.419 (5) Å, b = 12.793 (7) Å, c = 13.012 (4) Å, α = 61.10 (4), β = 91.42 (4), γ = 72.71 (4)°, V = 1143 (1) $Å^3$, and Z = 2.[9]

The data crystal displayed acceptable mosaicity for the θ–2θ scan technique. The Syntex $P\bar{1}$ autodiffractometer was equipped with a scintillation counter and a pulse height analyzer. Mo K$\bar{\alpha}$ radiation was monochromatized by using the 002 face of mosaic graphite. Scans were from 1.4° below the Mo Kα_1 peak to 1.1° above the MoKα_2 peak at a rate of 4°/min (2.4°/min for the second shell) in order to minimize the effects of decomposition. A collimator with a diameter of 1.5 mm was used as the crystal edges varied from ca. 0.6 to 1.1 mm. Data were collected in two concentric shells of 2θ, 0–40° and 40–50° with background time equalling 50% of the total scan time for the first shell and 75% for the second shell. The intensities of five standard reflections were monitored for every 95 reflections and showed on the average a total decrease of 10%, for which a correction was applied. A total of 4326 reflections were processed, yielding 3273 unique reflections which had intensities deemed above background ($I > 3\sigma(I)$). These were utilized in subsequent calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with empirical weights assigned by the method of Cruikshank.[10] The atomic scattering factors were taken from a recent tabulation, as were the anomalous dispersion terms for neodymium.[11] Calculations were undertaken by using the X-RAY 70 programs as well as a modified version of the Ibers program AGNOST for absorption correction.[12]

a Patterson synthesis. After refinement of its location, all 21 carbon atoms of the 2,4-dimethylpentadienyl ligands were located on a difference Fourier map. Least–squares refinement then led to an anisotropic agreement index ($R = \sum|F_o| - |F_c|/\sum F_o$) of 0.13 and a weighted index (Rw = $(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$) of 0.16. At this point an absorption correction was applied (μ(Mo Kα) = 22.90 cm^{-1} with the range of transmission coefficients being 0.207–0.465) for the unfortunately highly irregularly shaped crystal. Further refinement than led to convergence at R = 0.096 and R_w = 0.132. At this point, a number of highly disordered carbon (or oxygen) atom positions were becoming evident around the center of symmetry located at (0, 0.5, 0.5). At the nine highest locations were placed carbon atoms with occupancy factors of 0.25. In addition, despite 4326 reflections were processed, yielding 3273 unique reflections which high agreement indices, most of the hydrogen atoms of the 2,4-dimethylpentadienyl ligands could be located, and all were ultimately included in idealized locations (C–H = 0.95 Å) with an isotropic thermal parameter equal to 1.0 plus the equivalent isotropic thermal parameter of the carbon atom to which they were attached. Further refinement then led to final convergence at R = 0.088 and R_w = 0.125. An examination of the relative values of F_o and F_c revealed a clearly systematic variation as a function of Miller indices, which probably arose primarily from the irregular and therefore not well-modeled crystal shape. It appeared that an empirical correction could probably have been applied to reduce substantially the agreement indices. However, it was felt that the otherwise appealing result of lowered agreement indices was far outweighed by the danger of inaccurately biasing the data and hence the resulting conclusions to be made. Further, it was readily noted that most of the comparisons we desired to make could now be made on a statistically sound basis (differences > 3σ) and so no further attempts were made to modify the structural result. A final difference Fourier map revealed no peaks away from the neodymium atom greater than 0.94 e/$Å^3$ (This peak may have been solvent related). The standard deviation for the map was 0.20 e/$Å^3$. The final positional and thermal parameters obtained from the last cycle of least-squares refinement are presented in Table I, along with their estimated standard deviations. The positional and thermal parameters of the disordered ether atoms and the hydrogen atoms of the 2,4-dimethylpentadienyl ligands are available as supplementary material (Table II). The final values of 10F_o and 10F_c in electrons are also available as supplementary material. Reflections for which the measured intensity was less than zero were assigned zero values of F_o. Other than those mentioned later, intermolecular contacts are normal.

Results and Discussion

The reaction of anhydrous neodymium trichloride with 3 equiv of the potassium salt of the 2,4-dimethylpentadienyl anion (eq 1) leads to the formation of a bright

$$NdCl_3 + 3K(2,4\text{-}C_7H_{11}) \xrightarrow{THF} Nd(2,4\text{-}C_7H_{11})_3 + 3KCl \qquad (1)$$

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[9] The standard cell is a = 12.793 (7) Å, b = 13.012 (4) Å, c = 8.419 (5) Å, α = 91.42 (4)°, β = 107.29 (4)°, and γ = 118.90 (4)°. To convert from the given cell to the standard cell the matrix is $00\bar{1}/\bar{1}00/010$.

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Table I. Positional and Thermal Parameters for the Principle Atoms of $Nd(2,4\text{-}C_7H_{11})_3$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nd	0.30082 (9)	0.15377 (8)	0.17418 (7)	0.01126 (11)	0.00711 (7)	0.00559 (6)	−0.00274 (7)	−0.00047 (6)	−0.00266 (5)
CA(1)	0.5941 (26)	0.0391 (23)	0.3524 (21)	0.0199 (37)	0.0178 (29)	0.0149 (25)	0.0011 (26)	−0.0073 (24)	−0.0129 (24)
CA(2)	0.6351 (21)	−0.0342 (21)	0.2959 (19)	0.0095 (25)	0.0152 (26)	0.0102 (18)	−0.0035 (20)	0.0000 (17)	−0.0023 (17)
CA(3)	0.5303 (22)	−0.0957 (15)	0.2830 (15)	0.0187 (31)	0.0062 (14)	0.0072 (14)	−0.0008 (17)	−0.0042 (16)	−0.0023 (12)
CA(4)	0.3848 (23)	−0.1134 (16)	0.3295 (15)	0.0182 (31)	0.0077 (16)	0.0071 (14)	−0.0045 (18)	−0.0005 (17)	−0.0007 (12)
CA(5)	0.2928 (24)	−0.0537 (18)	0.3822 (17)	0.0200 (34)	0.0098 (18)	0.0090 (17)	−0.0050 (21)	0.0049 (20)	−0.0037 (15)
CA(6)	0.7930 (24)	−0.0491 (25)	0.2482 (22)	0.0123 (30)	0.0195 (33)	0.0144 (25)	−0.0046 (25)	0.0033 (22)	−0.0084 (24)
CA(7)	0.3233 (32)	−0.2024 (22)	0.3079 (25)	0.0281 (50)	0.0121 (24)	0.0172 (29)	−0.0093 (29)	0.0029 (30)	−0.0079 (23)
CB(1)	0.2840 (28)	0.4002 (16)	0.1129 (17)	0.0291 (44)	0.0066 (16)	0.0089 (17)	−0.0069 (22)	0.0015 (22)	−0.0021 (13)
CB(2)	0.3086 (26)	0.3394 (17)	0.2366 (18)	0.0253 (39)	0.0077 (16)	0.0106 (18)	−0.0041 (21)	−0.0007 (21)	−0.0057 (15)
CB(3)	0.2120 (20)	0.2658 (16)	0.3075 (15)	0.0142 (26)	0.0084 (16)	0.0086 (15)	−0.0045 (17)	−0.0004 (16)	−0.0035 (13)
CB(4)	0.0512 (21)	0.2587 (17)	0.2776 (15)	0.0139 (26)	0.0113 (19)	0.0079 (14)	−0.0030 (18)	0.0009 (15)	−0.0055 (14)
CB(5)	−0.0315 (21)	0.3040 (21)	0.1670 (16)	0.0120 (26)	0.0165 (25)	0.0087 (16)	−0.0030 (20)	0.0011 (16)	−0.0075 (17)
CB(6)	0.4505 (31)	0.3424 (20)	0.2997 (21)	0.0315 (50)	0.0111 (22)	0.0139 (24)	−0.0108 (28)	0.0003 (27)	−0.0072 (19)
CB(7)	−0.0215 (29)	0.1883 (25)	0.3865 (21)	0.0216 (40)	0.0174 (30)	0.0109 (21)	−0.0069 (29)	0.0055 (24)	−0.0063 (21)
CC(1)	0.4798 (23)	0.1590 (19)	−0.0073 (17)	0.0173 (31)	0.0125 (21)	0.0093 (16)	−0.0013 (20)	0.0076 (19)	−0.0060 (16)
CC(2)	0.3461 (22)	0.2721 (17)	−0.0670 (15)	0.0159 (29)	0.0093 (17)	0.0073 (14)	−0.0045 (18)	0.0008 (16)	−0.0025 (13)
CC(3)	0.1686 (21)	0.2889 (17)	−0.0688 (14)	0.0157 (28)	0.0102 (18)	0.0062 (13)	−0.0012 (18)	0.0008 (15)	−0.0038 (13)
CC(4)	0.0863 (20)	0.2011 (19)	−0.0286 (15)	0.0129 (26)	0.0143 (22)	0.0069 (13)	−0.0046 (19)	−0.0001 (15)	−0.0060 (15)
CC(5)	0.1676 (25)	0.0691 (18)	0.0426 (17)	0.0227 (36)	0.0113 (19)	0.0097 (17)	−0.0084 (22)	−0.0043 (20)	−0.0050 (15)
CC(6)	0.3784 (31)	0.3936 (21)	−0.1386 (19)	0.0302 (50)	0.0110 (22)	0.0092 (19)	−0.0106 (28)	0.0026 (24)	−0.0009 (16)
CC(7)	−0.1055 (25)	0.2553 (21)	−0.0647 (22)	0.0164 (34)	0.0111 (22)	0.0149 (25)	−0.0017 (22)	−0.0066 (23)	−0.0042 (19)

Table III. Electronic Spectral Data for $Nd(2,4\text{-}C_7H_{11})_3$

λ, nm	ε	λ, nm	ε
532	37	753	26
541	33	770	11
597	41	797	5.6
606	125	813	28
610	131	819	12
620	21	828	14
628	10	841	4.6
688	2.6	887	5.1
696	1.5		

green, air-sensitive crystalline compound, soluble in most organic solvents, and formulated as $Nd(2,4\text{-}C_7H_{11})_3$. The infrared spectrum of the product is devoid of both C=C bands and C—O bands due to coordinated THF and is somewhat similar to the spectrum of $Fe(2,4\text{-}C_7H_{11})_2$.[13] Flame and precipitation tests demonstrated the absence of both potassium and chlorine, while analytical data are consistent with the above formulation. A room-temperature magnetic moment of 3.58 μ_B was measured in THF, close to the free ion value of 3.68 for an f^3 system.[14] The proton NMR spectrum (see Experimental Section) displays the expected pattern of four resonances having relative intensities of 2:1:6:2. The electronic spectrum of this compound (Table III) exhibits the general pattern expected for the Nd(III) ion, although a noticeable enhancement of the extinction coefficients has taken place compared to their usual values of ca. 1–10. Such features have been also observed in a number of other organolanthanide spectra.[4,15] Also present are bands attributable to either ligand–metal charge transfer or ligand π–π^* excitations.[16] Collectively the above data provides a convincing case for the products formulation as $Nd(2,4\text{-}C_7H_{11})_3$, although the exact structural nature was still unclear. The reasonable solubility of the product in noncoordinating solvents suggested an unassociated structure such as known for $Sm(C_9H_7)_3$ (C_9H_7 = indenyl)[17] rather than an associated structure such as in $[Nd(CH_3C_5H_4)]_4$[18] or $[Sm(C_5H_5)_3]_\infty$[19]. The large size of a pentadienyl ligand would seem consistent with this notion, and on this basis a structural pattern based on three η^5-pentadienyl ligands was anticipated, in which the nine partially anionic carbon atoms could be occupying sites in a similar geometric fashion as that of the nine-coordinate tricapped trigonal prismatic $Nd(H_2O)_9^{3+}$ ion.[14,20] However, other structural patterns such as probably found in the known $Ln(C_5H_5)_2(C_3H_5)$[21] or $Ln(C_5H_5)_2(acac)$[21b,22] complexes could not be entirely excluded.

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(16) An absorption at 233 nm (ε 32000) may be attributed to a π–π^* transition. For comparison, $K^+(2,4\text{-}C_7H_{11}^-)$ also displayed this absorption at 233 nm (ε 12000). Some distortion of the bands may occur due to THF interference. A charge transfer transition may be obscured by the intense π–π^* band.

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Table IV. Selected Bond Distances (Å) and Angles (Deg) for Nd(2,4-C_7H_{11})$_3$

		Bond Distances			
Nd-CA(1)	2.800 (22)	Nd-CB(1)	2.808 (22)	Nd-CC(1)	2.817 (22)
Nd-CA(2)	2.859 (15)	Nd-CB(2)	2.873 (27)	Nd-CC(2)	2.847 (18)
Nd-CA(3)	2.766 (15)	Nd-CB(3)	2.726 (24)	Nd-CC(3)	2.755 (16)
Nd-CA(4)	2.836 (17)	Nd-CB(4)	2.862 (21)	Nd-CC(4)	2.853 (21)
Nd-CA(5)	2.748 (18)	Nd-CB(5)	2.839 (18)	Nd-CC(5)	2.793 (28)
CA(1)-CA(2)	1.420 (46)	CB(1)-CB(2)	1.383 (28)	CC(1)-CC(2)	1.356 (22)
CA(2)-CA(3)	1.404 (36)	CB(2)-CB(3)	1.437 (28)	CC(2)-CC(3)	1.441 (26)
CA(3)-CA(4)	1.412 (27)	CB(3)-CB(4)	1.441 (28)	CC(3)-CC(4)	1.393 (31)
CA(4)-CA(5)	1.351 (33)	CB(4)-CB(5)	1.338 (28)	CC(4)-CC(5)	1.388 (25)
CA(2)-CA(6)	1.480 (30)	CB(2)-CB(6)	1.454 (39)	CC(2)-CC(6)	1.494 (32)
CA(4)-CA(7)	1.519 (43)	CB(4)-CB(7)	1.529 (30)	CC(4)-CC(7)	1.507 (25)
		Bond Angles			
CMA-Nd-CMB	119.9 (3)	CMA-Nd-CMC	119.8 (4)	CMB-Nd-CMC	120.4 (3)
CA(1)-CA(2)-CA(3)	122.4 (19)	CB(1)-CB(2)-CB(3)	124.7 (23)	CC(1)-CC(2)-CC(3)	126.1 (19)
CA(2)-CA(3)-CA(4)	131.4 (22)	CB(2)-CB(3)-CB(4)	132.5 (15)	CC(2)-CC(3)-CC(4)	131.7 (16)
CA(3)-CA(4)-CA(5)	126.7 (23)	CB(3)-CB(4)-CB(5)	125.9 (17)	CC(3)-CC(4)-CC(5)	124.9 (16)
CA(1)-CA(2)-CA(6)	120.6 (26)	CB(1)-CB(2)-CB(6)	117.4 (21)	CC(1)-CC(2)-CC(6)	119.5 (19)
CA(3)-CA(2)-CA(6)	117.0 (27)	CB(3)-CB(2)-CB(6)	117.7 (18)	CC(3)-CC(2)-CC(6)	114.5 (15)
CA(3)-CA(4)-CA(7)	114.3 (21)	CB(3)-CB(4)-CB(7)	114.0 (17)	CC(3)-CC(4)-CC(7)	116.8 (16)
CA(5)-CA(4)-CA(7)	118.9 (21)	CB(5)-CB(4)-CB(7)	120.1 (20)	CC(5)-CC(4)-CC(7)	118.4 (20)

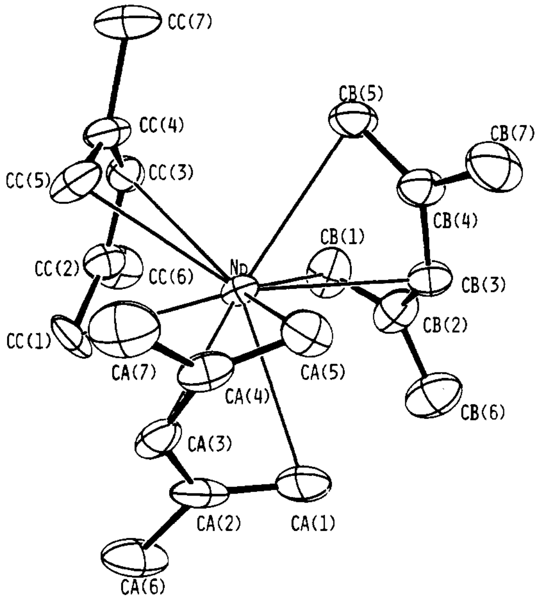

Figure 1. Perspective view and numbering scheme for the nonhydrogen atoms of Nd(2,4-C_7H_{11})$_3$. The 30% probability ellipsoids are shown.

The structural result of the X-ray diffraction study is presented in Figure 1 and 2 and clearly confirms the apparent pentahapto mode of bonding for the nearly planar pentadienyl ligands to the Nd(III) ions. In these figures, Nd–C bonds have only been drawn to those carbon atoms which are formally anionic. Although no crystallographic symmetry is imposed, the complex does nearly conform to idealized C_{3h} symmetry as a result of the head-to-tail orientations of the adjacent pentadienyl ligands. The extent to which the ligands are actually planar may be observed from the various least-squares planes presented in Table V. The planes listed in the first column demonstrate that the carbon atoms in the 2- and 4-positions are located out of the planes defined by the anionic 1-, 3-, and 5-positions by ca. 0.07 Å in a direction away from the Nd(III) ion. An alternative description (second column) is that the carbon atoms in the 3-positions are bent out of the planes formed by the 1-, 2-, 4-, and 5-carbon atom positions by ca. 0.10 Å. Finally, the third column indicates that when the 1-, 2-, 3-, 4-, and 5-carbon atom positions are used to define the ligand plane, the 1,5-carbon atom

Table V. Deviations (Å) of Atoms from Best Weighted Least-Squares Planes[a,b]

	I	II	III
CA(1)	0.000*	0.017*	0.008*
CA(2)	0.027	−0.021*	0.009*
CA(3)	0.000*	−0.086	−0.041*
CA(4)	0.095	0.022*	0.050*
CA(5)	0.000*	−0.018*	−0.026*
CA(6)	0.092	0.015	0.071
CA(7)	0.217	0.088	0.144
Nd	−2.280	−2.295	−2.295
	IV	V	VI
CB(1)	0.000*	−0.010*	−0.024*
CB(2)	0.114	0.012*	0.057*
CB(3)	0.000*	−0.132	−0.063*
CB(4)	0.070	−0.012*	0.032*
CB(5)	0.000*	0.010*	−0.003*
CB(6)	0.263	0.089	0.174
CB(7)	0.192	0.045	0.134
Nd	−2.285	−2.308	−2.309
	VII	VIII	IX
CC(1)	0.000*	0.003*	−0.006*
CC(2)	0.055	−0.004*	0.026*
CC(3)	0.000*	−0.089	−0.042*
CC(4)	0.070	0.004*	0.035*
CC(5)	0.000*	−0.003*	−0.012*
CC(6)	0.179	0.076	0.135
CC(7)	0.217	0.104	0.163
Nd	−2.292	−2.307	−2.307

[a] The displacements of those atoms which are used to define a given plane are designated by asterisks. Equations of planes: I, $2.009x - 4.381y + 6.667z = 3.372$; II, $2.018x - 3.874y + 7.158z = 3.553$; III, $2.067x - 4.144y + 6.853z = 3.473$; IV, $-2.147z + 10.782y + 6.655z = 4.457$; V, $-2.299x + 10.628y + 5.865z = 4.273$; VI, $-2.238x + 10.702y + 6.367z = 4.390$; VII, $0.181x + 6.586y + 12.995z = 1.039$; VIII, $0.047x + 6.971y + 12.978z = 1.039$; IX, $0.120x = 6.722y + 12.993z = 1.026$. [b] Interplanar dihedral angles (deg): I-IV, 61.59; I-VII, 59.62; IV-VII, 58.85; II-V, 60.17; II-VII, 59.71; V-VIII, 60.18; III-VI, 61.08; III-IX, 59.62; VI-IX, 59.35; I-II, 2.61; I-III, 1.13; II-III, 1.59; IV-V, 4.02; IV-VI, 1.54; V-VI, 2.51; VII-VIII, 2.67; VII-IX, 1.00; VIII-IX, 1.68.

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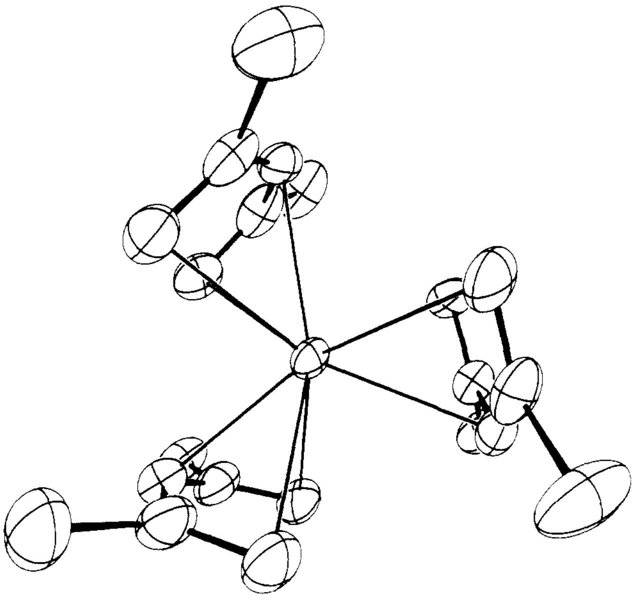

Figure 2. Perspective view of $Nd(2,4\text{-}C_7H_{11})_3$ down the idealized C_3 axis. The 40% probability ellipsoids are shown.

positions tend to lie ca. 0.01 Å toward the Nd(III) ion, while the carbon atoms in position 3 lie ca. 0.05 Å toward the Nd(III) ion, and the carbon atoms in the 2,4-positions lie ca. 0.035 Å away from the Nd(III) ion. With this last definition, the methyl groups are bent out of the ligand plane by an average of 3.9° away from the Nd(III) ion. In $Fe(2,4\text{-}C_7H_{11})_2$,[13] the bend was toward the Fe atom by 6–12°. The angles between various selected ligand planes are also contained in Table V, and it can be observed that the interligand planar angles are reasonably close to 60°, particularly for the second column. Alternatively one could look at the ligands as formed in various ways by two planar components. First, if one regards the ligand as "open envelopes", the fold angles between the planes formed by the 1, 2, 4, 5 and the 2, 3, 4 positions are respectively 6.8, 13.2 and 8.6° (averaging 9.5°). Second, if one looks at the ligands as derived from two overlapping allylic segments defined by the 1, 2, 3 and the 3, 4, 5 positions, the various fold angles are respectively 9.6°, 12.8, and 8.7°, averaging 10.4°. In the case it can be noted that the attached methyl groups are bent out the allylic planes by an average of 0.05 Å or 1.8° in a direction toward the Nd(III) ion. The relationship of the ligand nonplanarity to the relative Nd–C bond distances will be discussed subsequently.

The carbon-carbon bond distances within the pentadienyl ligands fall essentially in two sets. The first may be considered to be the internal set formed between the 2- and the 3-positions as well as the 3- and the 4-positions, while the external set may be defined as the bonds formed between the 1- and 2- positions as well as the 4- and the 5-positions. It can be observed that the external C–C bond distances average[23] 1.373 (12) Å, while the internal C–C bond distances average 1.421 (12) Å, a difference of 2.8 standard deviations which may be reasonably regarded as significant.[24] The origin of this difference may be readily understood by reference to the three resonance hybrids Ia, Ib, and Ic. While hybrids Ia and Ic would seem to shorten the internal and external C–C bond distances to a comparable extent, a contribution of hybrid Ib will preferentially shorten the external bonds, as is observed here and apparently also in $Fe(2,4\text{-}C_7H_{11})_2$. It can be noted that negative charge is localized somewhat more at the 3-position compared to 1,5-positions,[6] so that a reasonable contribution from hydrid Ib is to be expected. The CH_3-C(2 or 4) bond distances average 1.497 (13) Å. The inner-ligand C–C–C bond angles average 125.1 (8)° around the 2- or 4-positions, and 131.9 (10)° around the 3-positions. In comparison, for $Fe(2,4\text{-}C_7H_{11})_2$ these angles averaged 122.4 (5)° and 125.5 (3)°, respectively.[13] In each of these cases, then, the C2–C3–C4 angle is noticeably larger than the C1–C2–C3 or the C3–C4–C5 angles. It can be noted that in $Mn_3(3\text{-}C_6H_9)_4$ ($3\text{-}C_6H_9 = 3\text{-}CH_3C_5H_6$) just the opposite ordering is observed (ca. 126 vs. 121°).[25] The origin of the differences then seems to be the presence of a methyl group which causes a decrease in the interior C–C–C angle for the particular carbon atom to which it is attached.[26] Finally, it can be noted that even in this very heavy atom structure, it has been possible to locate most of the hydrogen atoms fairly clearly, although a relatively large degree of uncertainty must be associated with their locations. In this regard, the hydrogen atoms of the terminal CH_2 groups were found to lie more nearly in the ligand plane than had been observed in either $Fe(2,4\text{-}C_7H_{11})_2$ or $Mn_3(3\text{-}C_6H_9)_4$. This may partly be a result of higher ionic character and larger interior C-C-C bond angles of the ligand in this case which tends to separate the opposite CH_2 groups in the 1- and 5- positions and reduces H-H repulsions in a planar orientation.

The nature and geometry of the metal–ligand bonding is clearly of major interest. The ligands are fairly symmetrically located around the Nd(III) ion, with angles of 119.9 (3), 119.8 (4), and 120.4 (3)° being subtended by their center of masses (defined by atoms C(1)–C(5)). The Nd–(center of mass) distances are 2.372 (7), 2.375 (11), and 2.377 (10) Å, respectively, averaging 2.375 (5) Å. Perhaps the most appropriate description of the coordination geometry is that the Nd(III) ion is surrounded by nine partially anionic carbon atoms (to which bonds have been drawn) in a distorted tricapped trigonal prismatic array. It can be noted that the angles between the various Nd–C(1)–C(5) planes are nearly 120°, being 118.84° (ligands 1,2), 119.99° (ligands 1,3), and 120.57° (ligands 2,3), while the CA(3)–Nd–CB(3), CA(3)–Nd–CC(3), and CB(3)–Nd–CC(3) angles are 119.7 (5), 119.8 (6), and 120.5 (5)°, respectively. To produce a nearly symmetric tricapped trigonal prism, the two sets of bonds should be mutually staggered, with an angle of 60° subtended between them. However, since each of the central carbon atoms is a part of the same ligand as two terminal carbon atoms, the angle between each of the Nd–C(3) vectors and the corresponding Nd–C(1)–C(5) planes will be less than 60°, being

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[23] When average values are reported or discussed, the standard deviations of the mean are given in parenthesis.

[24] It can first be noted that all of the external C–C bonds are longer than 1.39 Å, while all but one (the most uncertain) of the internal C–C bonds are shorter than 1.39 Å. Second, it appears that the standard deviations of these distances may have been slightly over estimated. On the basis of their distributions, average C–C bond distances of 1.421 (9) and 1.373 (12) Å can be derived for the internal and external C–C bonds, respectively.

[25] Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.*, **1981**, *104*, 1120.

[26] The interior C–C–C angles in this structure are clearly larger than those observed either $Fe(2,4\text{-}C_7H_{11})_2$ or $Mn_3(3\text{-}C_6H_9)_4$. While there are 13 C–C nonbonded contacts in the range 3.33 (3)–3.44 (4) Å in the present structure that might be considered as a source of this difference,[27] it appears that the ligands in the iron and manganese complexes are actually contracted in order to increase the metal–ligand and hence ligand–ligand separations. It can also be noted for this structure that the contact distance between a given methyl group and the nearest two carbon atoms in the 1-, 3-, and/or 5-positions average 2.473 (10) Å.

[27] (a) The van der Waals radius for carbon in 1.7 Å.[27b] (b) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

43.70, 43.23, and 43.36° for ligands 1, 2, and 3, respectively (average = 43.4°). As a result, the angles between a given Nd–C(3) vector and the Nd–C(1)–C(5) plane of the adjacent ligand are 75.61 (ligands 1, 2), 76.29 (ligands 1, 3), 77.21° (ligands 2, 3), respectively (average = 76.4°). Thus, the geometry of the partially anionic carbon atoms may be viewed as a tricapped trigonal prism in which the three capping positions have been rotated 16.5° from their idealized locations.

Certainly most revealing about the bonding in this compound are the relative magnitudes of the Nd–C bond distances. While in the case of Fe(2,4-$C_7H_{11})_2$ the Fe–C distances were shortest to the 2- and 4-positions, in the present case the Nd–C distances are *longest* to the 2- and 4-positions, clearly indicating some profound differences in the bonding for the two systems. At least as important is the general indication that the somewhat flexible nature of the pentadienyl ligands can allow some useful comparisons regarding the general favorability of bonding of the various sites of the ligand. Indeed, in this case the average Nd–C(3) distance is the shortest at 2.749 (10) Å, with the Nd–C(1,5) distances intermediate at 2.801 (9) Å, and the Nd–C(2,4) distances longest at 2.855 (8) Å. The differences in these average distances are clearly significant statistically and precisely follow the known ordering of relative charge density, since charge is localized somewhat at the 3-positions and formally absent at the 2- and 4-positions.[6] The relative ordering of these distances is then clearly compatible with, and indicative of, the presence of a high degree of ionic character in the metal–ligand bonding. For purposes of comparison with other structures, however, a weighted average Nd–C bond distance of 2.81 (1) Å may be used. This distance is at the low end of the range of Nd–C bond distances (2.79–2.88 (2) Å) in what may be viewed as a formally ten-coordinate $[Nd(CH_3C_5H_4)_3]_4$ complex.[17] As a further comparison, $[Nd(C_8H_8)(THF)_2{}^+][Nd(C_8H_8)_2{}^-]$ contains several sets of Nd–C bond distances.[28] In the cation, the Nd–C bond distances averaged 2.79 (1) Å, while for the anion one ring engages in Nd–C bond distances which average 2.68 (1) Å, while the other ring (which partially bridges the cation) forms Nd–C bond distances averaging 2.79 (1) Å. Perhaps most useful as a comparison to the present case is the structure of the monomeric $Sm(C_9H_7)_3$ (C_9H_7 = indenyl) complex,[17] for which the Sm–C bond distances ranged from 2.68 (1) to 2.79 (1) Å, averaging 2.75 (1) Å. Taking into account the relative sizes of nine-coordinate Nd(III) and Sm(III) ions (1.30 vs, 1.27 Å),[29] one would predict an approximate nine-coordinate Nd–C bond distance of 2.78 Å. Thus, the distances observed here might seem to be a bit longer (by ca. 0.03 Å) than expected. This could well arise from the number of intramolecular nonbonded contacts observed on the coordination sphere and if so would seem to suggest that the single negative charges carried by either a pentadienyl or a cyclopentadienyl ligand act in otherwise approximately comparable extents in their abilities to bring their respective five-carbon ligand in close proximity to the ionic lanthanide metal ion.

Despite the above considerations, the nature and extent of the interaction between the Nd(III) ion and the formally uncharged carbon atoms in the 2- and 4-positions remains very much open to question. Since these carbon atoms have been bent out of the ligand plane in a direction away from the Nd(III) ion, the interaction would seem to be at least slightly repulsive at a distance of 2.85 Å, although the interaction could well be at least slightly attractive at a somewhat longer distance, presumably through a principally donor function for the ligand. While olefin complexes of transition metals generally utilize the ligand more as an acceptor than as a donor, complexes of Ag^+ tend to utilize the ligand more as a donor.[30] Such also must be the case in the certainly at least somewhat ionic $(C_6H_6)U(Cl_2AlCl_2)_3$ complex[31] and presumably as well in our own recent $(C_5(CH_3)_5)U(2\text{-}C_4H_7)_3$ π-allyl complex where U–C(1,3) = 2.66 (1) Å and U–C(2) = 2.80 (1) Å.[32] In this latter actinide π-allyl one can note a difference in U–C bond distances of 0.14 Å between charged and uncharged carbon atoms, a difference much greater than that observed in the present study of an even more ionic complex. This all may be ascribed to the relative differences between the allyl and pentadienyl ligands where an allyl ligand may remain planar and yet locate the uncharged carbon atom away from the metal by adopting more of an ylid-like geometry, while a nearly planar pentadienyl ligand having comparable M-C(1, 3, and 5) bond distances will necessitate a close interaction also with the carbon atoms in the 2- and 4-positions. Unfortunately, the results of the present study do not allow a more quantitative estimate of the interaction between the ionic lanthanide(III) ions and neutral unsaturated carbon centers. However, it is clear that these entities may be brought into close proximity, thus allowing for potential transformations to occur. Conceivably, the results of the present study could have a bearing on the anionic polymerizaton of olefins (particularly polyolefins),[33] as well as the bonding and (to date undertermined) structures of other interesting lanthanide–olefin or –acetylene compounds. Finally it can be noted that the pentadienyl complexes of the lanthanides have the potential for exhibiting a much higher degree of chemical versatility than most other lanthanide systems, as isomerizations to η^3, η^1, and η^2 (acac-like) bonding patterns would all seem feasible.

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and the positional and thermal parameters for the hydrogen atoms and the disordered ether molecules (23 pages). Ordering information is given on any current masthead page.

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