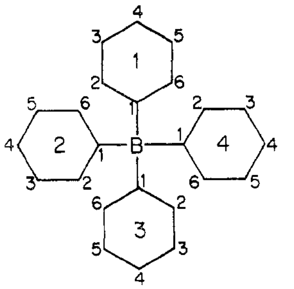
curately.[7] They range from ~1.12 to ~1.14 Å. In $Cu_3(NH_3)_3(CN)_4$[28] two of the three crystallographically different cyanide groups are disordered, but for the ordered cyanide C-N = 1.151 (9) Å. Perhaps the best bridging cyanide bond determination is to be found in the structure report[22] for $(NH_3)_5CoN\text{-}CCo(CN)_5 \cdot H_2O$. In this system the cyanide is ordered and C-N = 1.152 (5) Å. The terminal C-N bond lengths in this same compound range from 1.135 (5) to 1.154 (5) Å. Thus, considering the accuracy associated with our C-N = 1.127 (9) Å bond distance for $[Cu_2(tren)_2(CN)_2](BPh_4)_2$ and the range of C-N bond lengths for the variety of systems listed above as well as for other transition metal compounds (see references in ref 22), it is concluded that little is to be learned from C-N lengths in general and that this distance in our system is "normal."

Positional parameters, temperature factors, and bonding angles and distances for the tetraphenylborate anion are given in Tables IV-VI. The numbering scheme used is illustrated in the diagram



The general structural features of the tetraphenylborate in this system are similar to those found previously in others.[44,47] The ring angles at the site of boron binding are small (~114°), while those adjacent to this are large (~123°), and the boron atom lies out of the plane of each phenyl ring (see Table VII) by anywhere from 0.06 to 0.20 Å. The dihedral angles between the phenyl rings as usual show a wide range, apparently adjusting in order to pack most efficiently into the lattice.

In order to estimate the configuration stability of the tetraphenylborate anion, internuclear repulsion energies were calculated as described in previous publications.[44,47] These calculations sum the potential energy $U_{ij} = a_{ij}[\exp(-b_{ij}r_{ij})] - c_{ij}r_{ij}^{-6}$ over all C-H, C-C, and H-H pairs in the anion. When the total potential energy of the anion in this system is compared to that found[44] for $[Ni_2(tren)_2(NCO)_2](BPh_4)_2$, the difference is 3 kcal/mol with the copper system being less stable. This conformational instability of the tetraphenylborate may be taken as a reflection of the relative structural integrity of the $[Cu_2(tren)_2(CN)_2]^{2+}$ cation and the overall stability of the lattice packing.

Acknowledgments. We are very grateful for support from NIH Grant HL 13652 and for the guidance of Professor G. D. Stucky. Funds for computing were derived from the University of Illinois Research Board.

Registry No. $[Cu_2(tren)_2(CN)_2](BPh_4)_2$, 51464-43-8.

Supplementary Material Available. The final values of $|F_o|$ and $|F_c|$ for 2773 reflections will appear following these pages in the microfilm edition of this journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1911.

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Contribution from the Transuranium Research Laboratory,
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Crystal Structure of Neodymium Tris(methylcyclopentadienide)[1]

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The crystal structure of neodymium tris(methylcyclopentadienide) was determined by single-crystal X-ray diffraction methods. Crystals are monolinic, space group $P2_1/c$, and the unit cell dimensions are a = 14.257 (5) Å, b = 26.85 (1) Å, c = 9.286 (3) Å, β = 120° 17 (5)'; Z = 8. The structure was determined by Patterson and Fourier methods and was refined by the method of least squares to an agreement index of 0.040 using 3463 observations and 349 variables. Each Nd atom is η^5-bonded to three cyclopentadienide rings and η^1-bonded to another ring of an adjacent $(C_6H_7)_3Nd$ group. This sharing of a C atom between two Nd atoms is repeated in a manner which produces tetrameric units: $[(C_6H_7)_3Nd]_4$. The types of Nd-C bonds found in this structure are in accord with the idea that lanthanide-cyclopentadienide organometallic bonds are mainly ionic in nature.

Introduction

There has been interest in the nature of the bonding between 4f and 5f metals and aromatic organic ligands since Birmingham and Wilkinson[3] first prepared the cyclopentadienides of Sc and the lanthanide elements and Reynolds and Wilkinson[4] synthesized tris(cyclopentadienyl)uranium chloride. The chemical behavior of the former clearly indicated ionic bonding in it while the latter appeared somewhat covalent. These authors suggested that structural data would be useful in confirming this and for the latter assumed a structure in

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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(3) J. M. Birmingham and G. Wilkinson, *J. Amer. Chem. Soc.*, 78, 42 (1956).

(4) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 2, 246 (1956).

order to carry out molecular orbital calculations. Nevertheless, structural determinations were slow in appearing and, except for the approximate analysis[5] done on $U(C_5H_5)_3Cl$, none were reported until the last 4 years. In this period, however, several precise studies have been made of compounds between lanthanide and actinide elements and ligands containing the cyclopentadienyl and cyclooctatetraenyl ions. A review has been published[6] of all the structures reported through 1972.

The crystal structure of $Sm(C_5H_5)_3$, which is the prototype for all the tris(cyclopentadienides) of the lanthanides Pr to Tb as well as the synthetic elements Pu to Cf, was studied by Wong, Lee, and Lee.[7] The description of the (disordered) structure which they gave provided very little of use in visualizing or understanding of the bonding. For reasons discussed previously[6] it seems likely that their results were derived from a twinned crystal. In any case, further structure analyses were clearly needed.

In order to avoid the crystallographic problem of twinning or disorder and still examine the spatial relationship between conjugated C_5 rings and trivalent metal ions, the addition of substituents to the ring was employed. First, samarium tris(indenide), $(C_9H_7)_3Sm$, was prepared and analyzed.[8] In this compound isolated trigonal molecules were found with essentially η^5 (pentahapto) bonding between the Sm^{3+} ion and the pentagonal portion of the fused-ring systems. Subsequently, to obtain a substance more similar to the pure cyclopentadienide, rings with single methyl substituents were used for ligands; and the structure found is to be described here. From the many lanthanide elements which form compounds of this composition we used Nd because its size is near to that of Am and our ultimate objective is the study of bonding to transuranic elements.

Experimental Section

Preparation of Crystals. Neodymium tris(methylcyclopentadienide), $(C_6H_7)_3Nd$, was prepared essentially by the method of Reynolds and Wilkinson.[9] Anhydrous $NdCl_3$ was made by dissolving Nd_2O_3 in a mixture of pyridine and aqueous HCl, evaporating to dryness, and subliming away the excess pyridinium chloride at 300°. To this $NdCl_3$ was added an excess of sodium methylcyclopentadienide in tetrahydrofuran under an Ar atomosphere. The mixture was stirred 2 hr and let stand overnight. Then the solvent was pumped off, and the residue gradually heated at 0.02 Torr to 200° to sublime away the product. This was resublimed twice to produce blue-violet crystalline $(C_6H_7)_3Nd$ which melted at 163° (previously reported[9] 165°). The density measured by flotation was 1.68 g cm^{-3} ($d_{\text{calcd}} = 1.67$ for $Z = 8$). Crystals for X-ray diffraction study were selected and sealed in glass under an Ar atmosphere because of their sensitivity to air and moisture.

Data Collection and Reduction. Precession X-ray photographs showed the symmetry to be monoclinic and had systematic absences indicative of space group $P2_1/c$ ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The unit cell dimensions at 25° are $a = 14.257$ (5) Å, $b = 26.85$ (1) Å, $c = 9.286$ (3) Å, and $\beta = 120°\ 17\ (5)'$; these values were obtained by least-squares refinement using 12 Bragg angles precisely measured by a diffractometer. For this purpose and for recording intensities a computer-controlled Picker four-circle instrument was employed with Mo Kα (Nb filtered) radiation, λ_{α_1} 0.70926 Å. Intensities were measured by θ-2θ scanning with the background measured at each end of the scans and averaged. Scan ranges varied from 0.6 to 1.8°. The X-ray takeoff angle was 2°. The detector aperture was 0.6 cm^2 at 21 cm from the crystal. A reference reflection was measured hourly, and its intensity stayed within 5% of its mean value throughout the data collection period. All independent reflections out to $2\theta = 45°$ were measured.

The crystal used for intensity data was a plate, 0.013 cm thick, bounded by two trapezoidal faces of 0.026 cm in greatest dimensions. By describing the sample in terms of its six bounding planes, it was possible to calculate absorption corrections.[10,11] For this compound and Mo radiation the linear absorption coefficient was 34.2 cm^{-1}, and computed transmission factors ranged from 0.51 to 0.67. Application of these factors and the Lorentz and polarization corrections followed by normalization by interpolation between measurements of the reference reflections reduced the observations to a set of 3473 relative squared structure factors, F_o^2. The variances of these observations were taken to be $\sigma^2(F_o^2) = \sigma_c^2 + (0.03F_o^2)^2$, where σ_c^2 is the variance due to the counting statistics.

Determination and Refinement of the Structure

A Patterson map was calculated using the F_o^2 data and was easily interpreted to the extent of yielding atomic positions for two independent Nd atoms of the asymmetric unit of structure. These are in general positions 4(e) of space group $P2_1/c$. Subsequent Fourier syntheses phased on these two atoms were used to locate the 36 carbon atoms, which are also in general positions.

Refinement of these atomic coordinates and anisotropic thermal parameters was carried out by full-matrix least squares. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, in which $w = 1/\sigma^2(F_o^2)$ and the F_c's are the calculated structure factors. Atomic scattering factors[12] for neutral atoms were used and the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion[13] of the Nd atom were included. The refinement converged after a few cycles, and the agreement index, $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, reached 0.047; the standard deviation of an observation of unit weight, σ_1, was 1.57.

A difference Fourier map was then calculated in order to look for the 42 H atoms which had been ignored up to this time. About three-fourths of these were found in the difference map in the vicinity of expected positions. But the remaining H atoms were not apparent in the map and the ones found were somewhat ill defined, so it was decided to include H atoms in assumed positions for the structure factor calculations. The H atoms on the rings were assumed to lie in the plane of each ring at a radial distance of 1.0 Å. The methyl H atoms were taken to be trigonally disposed about the C–C axis and to have a C–H length of 1.0 Å and a H–C–H angle of 112°. The angle of rotation of the CH_3 about its trigonal axis was varied in the least-squares refinement. All H atoms were assigned isotropic B values of 5 Å^2.

After several cycles in which only the methyl groups were allowed to change, a final cycle varying all Nd and C parameters and the rotation angles of the CH_3 groups was carried out. This involved 3463 observations and 349 variables. (Ten reflections with $2\theta < 6°$ were omitted because of background uncertainties.) The final R index was 0.040 and $\sigma_1 = 1.265$. Following this refinement another difference Fourier map was computed and examined for the presence of H atoms at the assumed positions. As found previously only about two-thirds of those expected were discernible above background. Thus it appears that the H atoms in this compound have a detectable effect on the intensities, but these were not measured accurately enough to locate the atoms directly.

Refined positional and anisotropic thermal parameters for the Nd and C atoms are listed in Table I, and the assumed coordinates for the H atoms are in Table II. A table of observed and calculated structure factors is available elsewhere.[14]

Description and Discussion of the Structure

The basic structural unit in this crystal is the tetramer of

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(5) C. H. Wong, T. Yen, and T. Lee, *Acta Crystallogr.*, **18**, 340 (1965).

(6) J. H. Burns, Proceedings of the Tenth Rare Earth Research Conference, Carefree, Ariz., Apr 30–May 3, 1973, No. CONF-730402-P2, p 846.

(7) C. H. Wong, T. Lee, and Y. Lee, *Acta Crystallogr., Sect. B*, **25**, 2580 (1969).

(8) J. L. Atwood, J. H. Burns, and P. G. Laubereau, *J. Amer. Chem. Soc.*, **95**, 1830 (1973).

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(10) The computer programs used in this work and their accession numbers from the "World List of Crystallographic Computer Programs"[11] are as follows: ORDATLIB (No. 81), Ellison, *et al.*; ORXFLS3 (No. 84), Busing, *et al.*; ORFFE3 (No. 85), Busing, *et al.*; ORTEP2 (No. 83), Johnson. In addition, local versions of A. Zalkin's Fourier program by G. Brunton and of W. Hamilton's BSPLAN by G. Brown were employed.

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(12) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(13) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(14) See paragraph at end of paper regarding supplementary material.

Table I. Refined Positional and Anisotropic Thermal Parameters[a]

	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Nd(A)	0.15490 (3)	0.11580 (1)	0.52841 (4)	37.9 (3)	7.1 (1)	71.3 (7)	−0.2 (1)	24.0 (3)	−1.1 (2)
Nd(B)	−0.26278 (3)	0.09279 (2)	0.47806 (4)	31.6 (3)	9.7 (1)	80.6 (7)	1.1 (1)	24.2 (4)	1.6 (2)
C(1)	0.2637 (7)	0.1563 (4)	0.2525 (11)	88 (8)	26 (2)	213 (19)	3 (3)	97 (11)	12 (5)
C(2)	0.1605 (6)	0.1366 (3)	0.2386 (9)	64 (6)	15 (2)	96 (13)	6 (3)	48 (8)	8 (4)
C(3)	0.1270 (7)	0.0874 (3)	0.2189 (9)	100 (8)	12 (2)	80 (13)	7 (3)	60 (9)	3 (4)
C(4)	0.0242 (7)	0.0849 (3)	0.1996 (9)	74 (7)	18 (2)	80 (13)	−6 (3)	25 (8)	−3 (4)
C(5)	−0.0104 (7)	0.1334 (4)	0.2001 (9)	64 (7)	20 (2)	109 (14)	4 (3)	41 (8)	3 (4)
C(6)	0.0728 (6)	0.1657 (3)	0.2248 (9)	68 (7)	14 (2)	107 (14)	8 (3)	36 (8)	8 (4)
C(7)	0.4536 (9)	0.6991 (4)	0.2543 (13)	178 (14)	17 (2)	263 (25)	−21 (4)	−5 (15)	9 (6)
C(8)	0.4146 (7)	0.6506 (3)	0.2859 (10)	63 (7)	13 (2)	128 (15)	−5 (3)	−8 (9)	−7 (4)
C(9)	0.4625 (6)	0.6051 (4)	0.3033 (9)	40 (6)	25 (2)	101 (14)	2 (3)	−6 (7)	−6 (4)
C(10)	0.4026 (10)	0.5692 (4)	0.3483 (10)	136 (11)	14 (2)	75 (15)	−13 (4)	−38 (11)	0 (4)
C(11)	0.3239 (9)	0.5993 (6)	0.3530 (12)	100 (11)	40 (4)	110 (17)	−26 (5)	47 (11)	−8 (6)
C(12)	0.3315 (9)	0.6463 (6)	0.3153 (13)	78 (10)	38 (3)	175 (21)	−4 (5)	37 (11)	−36 (7)
C(13)	0.4310 (6)	0.3241 (3)	0.2486 (11)	52 (7)	20 (2)	241 (20)	7 (3)	57 (10)	5 (5)
C(14)	0.3191 (6)	0.3162 (3)	0.2199 (10)	58 (6)	10 (1)	157 (15)	4 (2)	48 (8)	5 (4)
C(15)	0.2364 (6)	0.2887 (3)	0.0903 (9)	70 (7)	9 (1)	147 (15)	4 (2)	50 (9)	4 (4)
C(16)	0.1449 (6)	0.2887 (3)	0.1116 (10)	62 (7)	8 (1)	159 (16)	−3 (2)	35 (8)	6 (4)
C(17)	0.1742 (6)	0.3156 (3)	0.2588 (10)	52 (6)	14 (2)	151 (15)	6 (2)	48 (8)	23 (4)
C(18)	0.2796 (6)	0.3326 (3)	0.3239 (9)	53 (6)	10 (1)	111 (13)	6 (2)	40 (7)	12 (3)
C(19)	0.1228 (7)	0.7794 (3)	0.3497 (12)	93 (9)	17 (2)	374 (27)	−5 (3)	131 (13)	−23 (6)
C(20)	0.0968 (6)	0.8317 (3)	0.3722 (10)	45 (6)	12 (2)	154 (15)	−3 (2)	40 (8)	−8 (4)
C(21)	0.0608 (6)	0.8699 (3)	0.2535 (9)	39 (6)	18 (2)	124 (14)	−7 (2)	25 (8)	−5 (4)
C(22)	0.0356 (6)	0.9107 (3)	0.3209 (10)	37 (6)	16 (2)	169 (16)	−1 (2)	29 (8)	3 (4)
C(23)	0.0551 (6)	0.8981 (3)	0.4776 (9)	45 (5)	15 (2)	151 (15)	−7 (2)	55 (8)	−16 (4)
C(24)	0.0928 (6)	0.8489 (3)	0.5103 (9)	51 (6)	12 (2)	156 (15)	−6 (2)	51 (8)	−3 (4)
C(25)	0.2907 (8)	0.8280 (4)	0.2006 (12)	109 (9)	25 (2)	260 (22)	−8 (4)	119 (12)	−21 (6)
C(26)	0.3167 (7)	0.8786 (3)	0.2820 (10)	72 (7)	16 (2)	151 (16)	−5 (3)	70 (9)	−12 (4)
C(27)	0.2557 (7)	0.9233 (4)	0.2170 (9)	68 (7)	20 (2)	116 (14)	−1 (3)	62 (9)	0 (4)
C(28)	0.3185 (8)	0.9618 (3)	0.3206 (11)	97 (8)	15 (2)	164 (17)	2 (3)	92 (11)	8 (4)
C(29)	0.4133 (7)	0.9418 (4)	0.4477 (11)	86 (8)	18 (2)	212 (19)	−12 (3)	99 (11)	−13 (5)
C(30)	0.4124 (7)	0.8918 (4)	0.4243 (11)	68 (7)	19 (2)	196 (18)	8 (3)	80 (10)	2 (5)
C(31)	0.2393 (6)	0.4540 (3)	0.4455 (9)	83 (7)	16 (2)	115 (14)	−1 (3)	46 (9)	−6 (4)
C(32)	0.2409 (6)	0.4598 (3)	0.2859 (8)	53 (6)	7 (1)	81 (12)	−3 (2)	25 (7)	−3 (3)
C(33)	0.3256 (5)	0.4451 (3)	0.2593 (8)	44 (6)	11 (1)	91 (13)	−4 (2)	25 (7)	−1 (3)
C(34)	0.3034 (6)	0.4611 (3)	0.1015 (9)	52 (6)	12 (1)	135 (14)	−2 (2)	41 (8)	−5 (4)
C(35)	0.2028 (6)	0.4870 (3)	0.0296 (8)	56 (6)	7 (1)	94 (12)	−6 (2)	24 (7)	2 (3)
C(36)	0.1635 (6)	0.4848 (3)	0.1422 (9)	54 (6)	9 (1)	109 (13)	−1 (2)	38 (7)	−7 (3)

[a] Temperature factors have the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table II. Assumed Positions for Hydrogen Atoms[a]

	x	y	z		x	y	z
H1a	0.330	0.139	0.343	H19a	0.085	0.755	0.384
H1b	0.265	0.151	0.147	H19b	0.100	0.772	0.231
H1c	0.273	0.193	0.278	H19c	0.202	0.772	0.417
H3	0.170	0.058	0.219	H21	0.054	0.869	0.142
H4	−0.018	0.054	0.186	H22	0.007	0.945	0.264
H5	−0.082	0.143	0.186	H23	0.044	0.920	0.554
H6	0.071	0.203	0.232	H24	0.113	0.830	0.614
H7a	0.520	0.711	0.356	H25a	0.315	0.825	0.118
H7b	0.472	0.696	0.164	H25b	0.326	0.801	0.284
H7c	0.398	0.726	0.220	H25c	0.211	0.821	0.140
H9	0.526	0.597	0.288	H27	0.182	0.926	0.116
H10	0.416	0.532	0.369	H28	0.298	0.998	0.306
H11	0.269	0.586	0.381	H29	0.472	0.961	0.541
H12	0.283	0.674	0.311	H30	0.471	0.868	0.498
H13a	0.487	0.307	0.353	H31a	0.217	0.420	0.458
H13b	0.439	0.311	0.155	H31b	0.312	0.460	0.546
H13c	0.451	0.360	0.259	H31c	0.187	0.478	0.452
H15	0.241	0.272	−0.002	H33	0.392	0.426	0.341
H16	0.073	0.273	0.037	H34	0.349	0.455	0.050
H17	0.126	0.322	0.307	H35	0.166	0.504	−0.081
H18	0.321	0.353	0.427	H36	0.093	0.499	0.123

[a] Each hydrogen is labeled according to the carbon atom to which it is attached.

$(C_6H_7)_3Nd$ molecules shown in Figure 1. Each Nd atom has three η^5-bonded C_5 rings and makes one η^1 bond to one of the rings which is η^5-bonded to another Nd atom. Thus the atoms C(23) and C(35) are each shared between two Nd atoms; this sharing plus that of their centrosymmetric equivalent atoms produces the tetramer. Between tetramers are only van der Waals contact distances typical of C and H atoms.

The eight molecules of the monoclinic unit cell are shown in Figure 2. In this figure each isolated molecule of $(C_6H_7)_3Nd$ is actually part of a tetramer extending into other cells.

There are six crystallographically independent CH_3-C_5H_4 ligands. In each, the pentagonal ring of C atoms is essentially planar, and the best least-squares planes describing them are given in Table III along with distances of the atoms from them. The C-C bond lengths are listed in Table IV. The mean C-C length in each independently determined C_5 ring agrees quite well with the others and with known values for conjugated systems, although there are appreciable deviations of individual C-C lengths in two or three instances. Similar (or larger) variations have been observed in virtually all the reported cyclopentadienyl structures and are usually considered to be of no chemical significance unless they occur in the proper place in a ring which is σ-bonded to a metal causing the ring to have a diene configuration.[15] This is not the case here, and the variations probably result from systematic errors in the data. The bonds from the methyl C atoms to the rings are longer, as expected, and all six are very close in magnitude. The angles found in the six dependent rings are shown in Table V. The interior angles do not differ much from 108°, the value for a regular pentagon, and the exterior angle from ring to methyl group is near the ideal 126° in each case. The thermal motion, depicted by

(15) J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, 93, 3592 (1971); J. L. Calderon, F. A. Cotton, and P. Legzdins, *ibid.*, 91, 2528 (1969); F. W. B. Einstein, M. M. Gilbert, and D. G. Tuck, *Inorg. Chem.*, 11, 2832 (1972).

Table III. Least-Squares Planes and Deviations

	C_2-C_6	C_8-C_{12}	C_{14}-C_{18}	C_{20}-C_{24}	C_{26}-C_{30}	C_{32}-C_{36}
Parameters in $Ax + By + Cz - D = 0$ with Fractional Crystal Coordinates						
A	−1.80	2.29	−1.08	12.19	11.71	4.46
B	1.79	5.05	22.45	8.85	3.57	23.08
C	8.53	7.02	−4.00	−0.79	−8.29	1.78
D	1.49	6.24	5.87	8.24	4.50	12.18
Distance of Ring Carbons from Planes, Å						
	(2) 0.007	(8) 0.001	(14) 0.002	(20) 0.003	(26) 0.006	(32) 0.010
	(3) −0.010	(9) 0.000	(15) −0.005	(21) −0.002	(27) −0.009	(33) −0.001
	(4) 0.009	(10) −0.001	(16) 0.007	(22) −0.000	(28) 0.008	(34) −0.009
	(5) −0.005	(11) 0.002	(17) −0.005	(23) 0.001	(29) −0.004	(35) 0.015
	(6) −0.002	(12) −0.002	(18) 0.002	(24) −0.002	(30) −0.001	(36) −0.015
Distances of Methyl Carbons from Planes, Å						
	(1) −0.097	(7) 0.121	(13) −0.046	(19) −0.122	(25) 0.198	(31) 0.151
Distances of Metals from Planes, Å						
	(A) 2.530	(B) −2.490	(A) 2.473	(B) 2.577	(B) −2.507	(A) −2.576

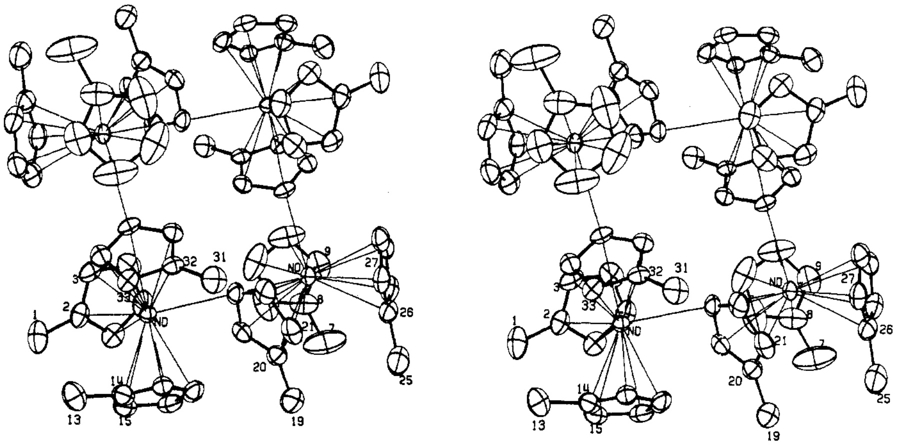

Figure 1. A stereoscopic pair of drawings depicting one tetrameric unit of the $Nd(C_6H_7)_3$ structure. Atoms are represented by their thermal ellipsoids. The numbering of the C atoms proceeds around each ring and corresponds to that used in Table I. H atoms are not included.

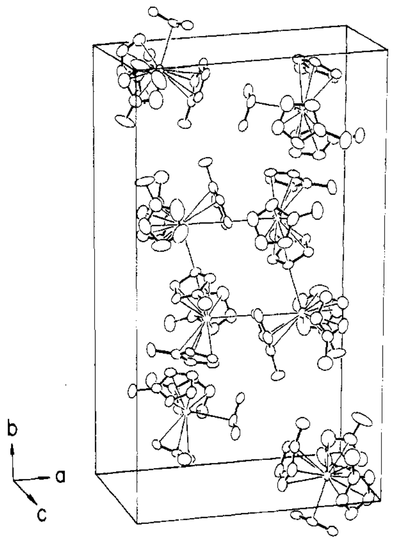

Figure 2. One unit cell of the structure of $(C_6H_7)_3Nd$.

the ellipsoids of Figure 1, suggests that the rings are librating about their fivefold axes and that the methyl substituents undergo a wagging motion of somewhat larger magnitude.

From the Nd-C distances given in Table VI, it is concluded that each Nd atom is equally bonded to all five C atoms of three rings. The interactions Nd(A)-C(23) and Nd(B)-C(35) are at distances about 0.2 Å greater than the average of the η^5 bonds and about 0.1 Å greater than the longest of them but are short enough to be considered η^1 bonds; the next nearest Nd-C distance is 3.5 Å.

Table IV. C-C Bond Lengths (Å)

Atoms	Length	Atoms	Length	Atoms	Length
Methyl Carbons					
1, 2	1.506 (11)	7, 8	1.502 (12)	13, 14	1.494 (10)
19, 20	1.492 (11)	25, 26	1.506 (11)	31, 32	1.502 (9)
Ring Carbons					
2, 3	1.386 (11)	8, 9	1.369 (12)	14, 15	1.397 (10)
3, 4	1.385 (11)	9, 10	1.479 (13)	15, 16	1.414 (10)
4, 5	1.395 (11)	10, 11	1.401 (15)	16, 17	1.410 (11)
5, 6	1.390 (11)	11, 12	1.329 (16)	17, 18	1.385 (10)
6, 2	1.425 (10)	12, 8	1.349 (13)	18, 14	1.412 (10)
Mean	1.396 (8)	Mean	1.385 (26)	Mean	1.404 (6)
20, 21	1.401 (11)	26, 27	1.425 (12)	32, 33	1.405 (9)
21, 22	1.394 (11)	27, 28	1.389 (11)	33, 34	1.401 (9)
22, 23	1.379 (10)	28, 29	1.379 (12)	34, 35	1.421 (10)
23, 24	1.401 (10)	29, 30	1.358 (12)	35, 36	1.415 (9)
24, 20	1.391 (10)	30, 26	1.384 (11)	36, 32	1.401 (9)
Mean	1.393 (4)	Mean	1.387 (11)	Mean	1.409 (4)

The structure of $(C_6H_7)_3Nd$ described here agrees well with the concept that lanthanide cyclopentadienides are mainly ionic compounds;[3,16] *i.e.*, the bonding between the metal and each conjugated ring is electrostatic. The η^5 bonding in this compound is, of course, typical of the covalent sandwich compounds, yet it also provides the most stable configuration for a purely coulombic interaction. On the other hand, the at-

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(16) L. J. Nugent, P. G. Laubereau, G. K. Werner, and K. L. Vander Sluis, *J. Organometal. Chem.*, 27, 365 (1971).

Table V. C–C–C Bond Angles (deg)

Atoms	Angle	Atoms	Angle	Atoms	Angle
1, 2, 3	127.0 (7)	7, 8, 9	125.9 (10)	13, 14, 15	126.2 (7)
2, 3, 4	109.6 (7)	8, 9, 10	106.9 (9)	14, 15, 16	108.5 (7)
3, 4, 5	107.9 (8)	9, 10, 11	102.7 (9)	15, 16, 17	107.0 (6)
4, 5, 6	108.1 (7)	10, 11, 12	111.4 (11)	16, 17, 18	108.5 (7)
5, 6, 2	108.0 (7)	11, 12, 8	109.4 (11)	17, 18, 14	108.5 (7)
6, 2, 3	106.4 (7)	12, 8, 9	109.6 (10)	18, 14, 15	107.4 (7)
6, 2, 1	126.3 (8)	12, 8, 7	124.3 (10)	18, 14, 13	126.3 (7)
19, 20, 21	126.7 (8)	25, 26, 27	127.1 (8)	31, 32, 33	125.9 (6)
20, 21, 22	107.3 (7)	26, 27, 28	106.9 (7)	32, 33, 34	109.7 (6)
21, 22, 23	108.7 (7)	27, 28, 29	108.3 (8)	33, 34, 35	106.5 (6)
22, 23, 24	108.1 (7)	28, 29, 30	108.8 (8)	34, 35, 36	108.3 (6)
23, 24, 20	107.6 (7)	29, 30, 26	109.3 (8)	35, 36, 32	107.9 (6)
24, 20, 21	108.3 (7)	30, 26, 27	106.6 (8)	36, 32, 33	107.5 (6)
24, 20, 19	124.7 (8)	30, 26, 25	125.7 (8)	36, 32, 31	126.3 (6)

Table VI. Nd–C Bond Lengths (Å)

Atoms	Length	Atoms	Length
Nd(A)–C(2)	2.789 (7)	Nd(B)–C(8)	2.784 (8)
C(3)	2.801 (7)	C(9)	2.746 (7)
C(4)	2.783 (7)	C(10)	2.732 (8)
C(5)	2.798 (8)	C(11)	2.746 (9)
C(6)	2.790 (7)	C(12)	2.784 (10)
Nd(A)–C(14)	2.789 (7)	Nd(B)–C(20)	2.886 (7)
C(15)	2.753 (7)	C(21)	2.875 (7)
C(16)	2.703 (7)	C(22)	2.808 (7)
C(17)	2.730 (7)	C(23)	2.786 (7)
C(18)	2.772 (7)	C(24)	2.841 (7)
Nd(A)–C(32)	2.895 (7)	Nd(B)–C(26)	2.805 (7)
C(33)	2.816 (7)	C(27)	2.815 (7)
C(34)	2.784 (7)	C(28)	2.788 (8)
C(35)	2.841 (7)	C(29)	2.727 (8)
C(36)	2.881 (7)	C(30)	2.738 (7)
Nd(A)–C(23)	2.990 (7)	Nd(B)–C(35)	2.978 (7)

traction of one out of three rings to two Nd atoms simultaneously without any observed effect (*via* bond lengths) on its delocalized electron system definitely suggests ionic rather than covalent bonding.

The size of the central metal ion in $(C_6H_7)_3Nd$ and in other tris(cyclopentadienides) is important in determining the number of rings bonded to it. The previously described sharing of rings causes each Nd ion to have 16 C atoms in its coordination sphere. This requirement for more than just the stoichiometric number of rings in the first coordination sphere has been seen in other compounds containing the larger radius lanthanides and actinides. The reported structure[7] for $(C_5H_5)_3Sm$ has four C_5 rings associated with each metal ion, in various configurations; this same structure type was found[17] for the tris(cyclopentadienides) of Pr to Tb and Pu to Cf. Another relevant structure[18] is that of $(C_5H_5)_3Pr{\cdot}CNC_6H_{11}$ in which there are three η^5-bonded rings and an additional C atom from the isocyanide molecule in the coordination sphere. The Ho analog has the same structure.[19] In the case of $(C_9H_7)_3Sm$[8] there are only three η^5-bonded rings around the Sm atom, but the failure to include more is attributed to the hindrance by the C_6 rings to each pentagon. In $(C_5H_5)_3Sc$,[20] containing the much smaller Sc ion, there are only 12 C atoms in the coordination sphere.

Hence the structural evidence so far accumulated on lanthanide cyclopentadienides points to the ionic model of bonding in that the spatial relationships observed are explainable as resulting from attaining the maximum number of cation–anion contacts compatible with their sizes and shapes.

Registry No. $[(C_6H_7)_3Nd]_4$, 51731-14-7.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfilm, referring to code number INORG-74-1916.

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