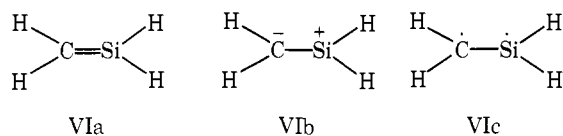


Considering the three electronic structures



proposed earlier on the basis of reactivity of substituted silaethylenes, it is interesting to note that pair VIa,VIb is in agreement with the electron distribution of Va and the pair VIb,VIc with that of Vb. If indeed, the energy of the lowest singlet is close to that of the lowest triplet, as the present calculations indicate, then at room temperature both  $S_0$  and  $T_1$  are populated and as far as overall reactivity is concerned all three electronic structures proposed earlier<sup>6</sup> are correct.

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## Crystal and Molecular Structure of a Novel Asymmetrical Neodymium-Cyclooctatetraene Compound, Cyclooctatetraenylbis(tetrahydrofuran)-neodymium(III) Bis(cyclooctatetraenyl)neodymate(III)

Sir:

In this communication we wish to report the preparation and crystal structure of a novel asymmetrical neodymium-cyclooctatetraene compound,  $[\text{Nd}(\text{C}_8\text{H}_8)(\text{OC}_4\text{H}_8)_2][\text{Nd}(\text{C}_8\text{H}_8)_2]$ . Lanthanide metal atoms, prepared by high temperature vacuum evaporation,<sup>1</sup> were codeposited with cyclooctatetraene at  $-196^\circ\text{C}$ . The reaction appeared to take place at  $-196^\circ\text{C}$  to yield a new class of organolanthanides,  $\text{Ln}_2(\text{COT})_3$ , which show chemical and physical properties similar to the well-known compounds  $\text{U}(\text{COT})_2$  and  $\text{KLn}(\text{COT})_2$  prepared by Streitwieser et al.<sup>2</sup> The Nd mem-

Table I. Summary of Crystal Data

Molecular formula:	$[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$
Molecular weight:	745.13
Linear absorption coefficient, $\mu$ :	$33.18\text{ cm}^{-1}$
Observed density: <sup>a</sup>	$1.75\text{ g/cm}^3$
Calculated density:	$1.71\text{ g/cm}^3$
Crystal dimensions:	$0.3 \times 0.08 \times 0.08\text{ mm}$
Space group:	$P2_1/c$ , monoclinic
Molecules/unit cell:	4
Cell constants:	$a = 16.664(3)$ , $b = 12.778(3)$ , $c = 14.347(4)\text{ \AA}$ ; $\beta = 108.90(2)^\circ$
Cell volume:	$2894.74\text{ \AA}^3$

<sup>a</sup> Experimental density measurements were obtained by flotation measurements in  $\text{CCl}_4\text{-CBr}_4$ .

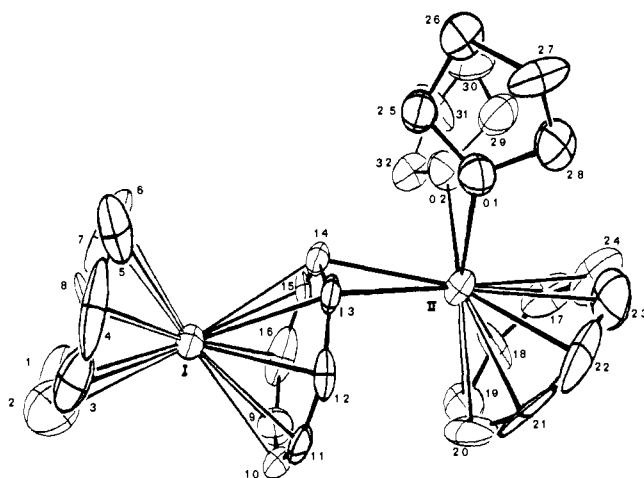


Figure 1. An ORTEP drawing of  $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$  approximately along the C axis.

ber of this series was purified by Soxhlet extraction into THF. Bright green crystals of  $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$  grew during the extraction.

Several crystals were sealed in thin-walled glass capillaries under a nitrogen atmosphere for x-ray diffraction analysis. The crystal chosen for study was mounted on a Syntex  $P\bar{1}$  computer-controlled four-circle diffractometer. Data were measured out to  $2\theta = 45^\circ$  using a  $\theta$ - $2\theta$  scan mode and monochromatic  $\text{Mo K}\alpha$  radiation. Crystal data are shown in Table I. The structure was refined with full-matrix least-squares methods using 3351 independent and nonzero reflections. No absorption corrections were made. The structure was solved by MULTAN. Following an anisotropic least-squares fit on all 36 nonhydrogen atoms, refinement on the 1371 independent reflections with  $F^2 > 3\sigma(F^2)$  is 3.30%. Positional parameters are presented in Table II.

The molecular structure consists of an anion-cation pair,  $[\text{Nd}(\text{COT})_2]^-$  and  $[\text{Nd}(\text{COT})(\text{THF})_2]^+$ , as shown in Figure 1. The anion is composed of  $\text{Nd}_I$  and COT rings 1 and 2. The carbons in ring 1 are numbered 1-8, while those in ring 2 are numbered 9-16. The cation is composed of  $\text{Nd}_{II}$ , COT ring 3, and two THF rings.

In rings 1, 2, and 3, the average bond distances are 1.384 (51), 1.419 (14), and 1.407 (25)  $\text{\AA}$  while the average angles are  $134.79(2.25)$ ,  $134.86(0.65)$ , and  $134.90(1.45)^\circ$ , respectively. All the carbon atoms lie within 0.035, 0.048, and 0.026  $\text{\AA}$  of the least-squares planes of their respective rings. These data demonstrate the ten  $\pi$ -electron aromatic nature of the  $\text{COT}^{2-}$  rings in this structure. The bond distances and interior angles of the THF rings agree well with those found in  $[\text{Ce}(\text{COT})\text{Cl}2\text{THF}]_2$ .<sup>3</sup>

The coordination sphere about  $\text{Nd}_I$  consists of ring 1 with an average Nd-C distance of 2.660 (24)  $\text{\AA}$  and ring 2 with an average Nd-C distance of 2.787 (19)  $\text{\AA}$ . The coordina-

**Table II.** List of Atomic Positions

Atom	X	Y	Z	Atom	X	Y	Z
Nd <sub>I</sub>	0.5194	0.2426	0.1085	C(17)	0.9403	0.2922	0.0505
Nd <sub>II</sub>	0.8282	0.3143	0.1498	C(18)	0.8743	0.2168	0.0152
C(1)	0.3581	0.1893	0.0151	C(19)	0.8343	0.1381	0.0490
C(2)	0.3697	0.1549	0.1084	C(20)	0.8408	0.1080	0.1456
C(3)	0.4030	0.1948	0.1939	C(21)	0.8988	0.1415	0.2478
C(4)	0.4342	0.2912	0.2350	C(22)	0.9628	0.2255	0.2778
C(5)	0.4509	0.3892	0.1933	C(23)	0.9939	0.2984	0.2294
C(6)	0.4456	0.4167	0.1059	C(24)	0.9906	0.3262	0.1407
C(7)	0.4136	0.3932	0.0104	O(1)	0.8467	0.4666	0.2735
C(8)	0.3778	0.2850	-0.0262	C(25)	0.7827	0.5492	0.2671
C(9)	0.6056	0.1086	0.0227	C(26)	0.8308	0.6396	0.3324
C(10)	0.6177	0.0659	0.1160	C(27)	0.9021	0.5794	0.4096
C(11)	0.6498	0.1061	0.2101	C(28)	0.9271	0.4916	0.3532
C(12)	0.6777	0.2038	0.2525	O(2)	0.8143	0.4845	0.0511
C(13)	0.6815	0.3077	0.2158	C(29)	0.8779	0.5699	0.0773
C(14)	0.6628	0.3570	0.1189	C(30)	0.8471	0.6503	-0.0013
C(15)	0.6421	0.3144	0.0269	C(31)	0.7969	0.5915	-0.0899
C(16)	0.6167	0.2111	-0.0141	C(32)	0.7707	0.4884	-0.0549

tion sphere about Nd<sub>II</sub> consists of ring 3, average Nd-C distance of 2.673 (16) Å, together with the two THF oxygen atoms, average Nd-O distance of 2.577 (11) Å, and part of ring 2. In particular C(14) is definitely in the coordination sphere of Nd<sub>II</sub> and C(13) and C(15) may well be. The Nd<sub>II</sub>-C(14) distance is 2.700 (18) Å while those of Nd<sub>II</sub>-C(13) and Nd<sub>II</sub>-C(15) are 2.896 (20) and 3.059 (19) Å, respectively.

The geometry of the Nd(COT)<sub>2</sub><sup>-</sup> anion is unique for all known lanthanide and actinide COT compounds.<sup>3-6</sup> The 0.1 Å difference in the average Nd-C distances for rings 1 and 2 and the 8.25° angle of intersection between the planes of rings 1 and 2 make the anion the first example of a lanthanide or actinide asymmetric M(COT)<sub>2</sub> unit. Also the position of ring 2 relative to Nd<sub>II</sub> is the first example of a lanthanide or actinide asymmetrically bonded to a COT<sup>2-</sup> ring. This additional coordination is, however, known for lanthanide cyclopentadienide compounds. For example, the crystal structure of neodymium tris(methylcyclopentadienide) shows both  $\eta_1$  Nd-C and  $\eta_5$  Nd-C interactions.<sup>7</sup> The  $\eta_1$  Nd-C bond lengths, 2.990 and 2.978 Å, are about 0.2 Å greater than the average of the  $\eta_5$  bonds. Both Sc(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub><sup>8</sup> and Sm(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub><sup>9</sup> also show  $\eta_5$  and  $\eta_1$  metal cyclopentadienide coordination.

Other interesting features are noted in comparing the three COT<sup>2-</sup> rings. Values of the standard deviation of bond lengths and angles, thermal parameters, and root-mean-square amplitudes of vibration are much less for ring 2 than for rings 1 and 3. Average standard deviations of the bond lengths and angles in ring 2 are 0.014 Å and 0.69° while in rings 1 and 3 they are 0.057 Å and 2.29° and 0.025 Å and 1.49°, respectively. Thermal parameters for ring 2 are only about one-half as large as the corresponding parameters for rings 1 and 3. The root-mean-square amplitudes of vibration for ring 2 are 0.137, 0.206, and 0.280 Å, while in rings 1 and 3 they are 0.139, 0.236, and 0.540 Å, and 0.138, 0.273, and 0.446 Å, respectively. These data clearly show that ring 2 is much more rigidly fixed in space than are rings 1 and 3. This does not seem surprising when one considers that ring 2 is asymmetrically bonded to Nd<sub>II</sub> while rings 1 and 3 are both symmetrically bonded to the neodymiums.

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#### Effect of Irradiation with Ultraviolet Light on Spectral Sensitization of the Photoelectrochemical Process of a Zinc Oxide Single-Crystal Electrode

Sir:

A number of reports have dealt with the spectral sensitization of photoelectrochemical reactions with dye molecules using semiconductor electrodes.<sup>1-12</sup> For n-type semiconductor electrodes, when a sensitizing dye is added to the electrolyte solution, an increase in the anodic photocurrent occurs upon irradiation in the longer wavelength regions. These photocurrents show a spectral dependence which follows the absorption spectrum of the sensitizer. Two different mechanisms, one involving electron transfer and another involving energy transfer, have been proposed for the electrochemical spectral sensitization<sup>1,4,9</sup> as well as for silver halide photography.<sup>13-15</sup> The sensitized anodic photocurrent at a ZnO single-crystal electrode has been attributed predominantly to electron transfer from the excited dye molecule to the conduction band of ZnO.<sup>2,5-7,10-12</sup>