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## MOLECULAR AND CRYSTAL STRUCTURE OF THE ADDUCT OF CYCLOHEXYLISONITRILE AND PRASEODYMIUM TRICYCLOPENTADIENIDE

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### Summary

The crystal structure of  $(C_5H_5)_3Pr \cdot CNC_6H_{11}$  was determined from single-crystal X-ray diffraction data. The monoclinic unit cell of dimensions  $a = 8.298(3)$ ,  $b = 21.66(1)$ ,  $c = 11.943(4)$  Å, and  $\beta = 104.98(3)^\circ$  contains four molecules in general positions of space group  $P2_1/c$ . Each molecule is composed of three  $C_5H_5$  rings in a nearly exact trigonal array,  $\eta^5$ -bonded to the Pr atom at a distance of 2.53 Å to the centroid of each ring, plus a single  $CNC_6H_{11}$  adduct attached to the Pr atom along the trigonal axis at 2.65 Å. The presence of a  $C\equiv N$  triple bond in the isonitrile moiety and the nearly linear  $C\equiv N-C$  configuration add credence to the previous proposal that there is a pure donor bond from the isonitrile carbon to the metal atom.

### Introduction

The tricyclopentadienides of lanthanide and actinide elements are Lewis acids, and many donor molecules have been found which form adducts with them; some examples of these are  $Yb(C_5H_5)_3 \cdot NH_3$  [1],  $Tb(C_5H_5)_3 \cdot OC_4H_8$  [1], and  $U(C_5H_5)_3 \cdot l$ -nicotine [2]. The most widely studied series of adducts are those with cyclohexylisonitrile ( $C_6H_{11}CN$ ), and complexes with the general formula  $(C_5H_5)_3M \cdot CNC_6H_{11}$  have been prepared for cases where M is any of the lanthanide elements (except Pm) or any actinide from U to Am [1,3].

From the infrared spectra of some of these latter compounds Fischer and Fischer [1] concluded that the molecular structure consists of three pentagonal rings centrally bonded to the metal ion plus the molecule of base attached to the metal ion by a  $\sigma$  donor bond from the isonitrile carbon atom. Proton nuclear magnetic resonance studies of  $(C_5H_5)_3Pr \cdot CNC_6H_{11}$  by von Ammon, et al. [4] confirmed this geometry and showed that, in toluene solution, the cyclohexyl chair is rapidly changing between the equatorial and axial positions at  $30^\circ C$ , slowly changing at  $-70^\circ C$ , and that the  $Pr-C\equiv N-C$  arrangement is nearly linear. The free energy of the conformational change and the equilibrium

constant were evaluated, and at  $-70^{\circ}\text{C}$  the equatorial form is favored over the axial one by about 2 : 1. Benjamin, et al. [5], using NMR measurements of benzene solutions at  $36^{\circ}\text{C}$ , obtained results in good agreement with these.

The structure determination by X-ray diffraction to be described here was performed to verify the inferences about molecular geometry from the above mentioned, less direct, methods and to provide quantitative measures of bond lengths and angles. Moreover, knowledge of this crystal structure was needed to further the understanding of the nature of the bonding in other tricyclopentadienides, for which only a limited number of structure determinations are available [6,7].

## Experimental

The compound was prepared by reaction of  $(\text{C}_5\text{H}_5)_3\text{Pr}$  and  $\text{CNC}_6\text{H}_{11}$  in dry benzene solution as previously described [1]. It was purified by evaporation of benzene and extraction of the solid product with dry pentane; green needles of  $(\text{C}_5\text{H}_5)_3\text{Pr} \cdot \text{CNC}_6\text{H}_{11}$  separated from the extractant. Suitable specimens for X-ray diffraction study were selected in an inert-gas box and sealed in thin-walled glass tubes for protection from air and moisture.

Precession X-ray photographs showed the crystals to have monoclinic symmetry with the  $c$  axis along the needle, and systematic absences ( $h0l$ , when  $l$  is odd and  $0k0$ , when  $k$  is odd) were indicative of space group  $P2_1/c$ . Measurements of  $2\theta$  angles for twelve reflections in the range  $36-40^{\circ}$ , using  $\text{Mo-K}\alpha$  radiation and a four-circle diffractometer, enabled us to get the best estimate of the unit-cell dimensions by the method of least squares. At  $23^{\circ}\text{C}$  these are:  $a = 8.298(3)$ ,  $b = 21.66(1)$ ,  $c = 11.943(4)$  Å, and  $\beta = 104.98(3)^{\circ}$ . The calculated crystal density is  $1.426 \text{ g cm}^{-3}$  for four molecules in the unit cell.

X-ray intensity data were collected using a computer-controlled Picker diffractometer and unfiltered  $\text{Mo-K}\alpha$  radiation. All the symmetry-independent reflections with  $2\theta \leq 45^{\circ}$  were measured with a scintillation-counter detector by the  $\theta - 2\theta$  scan method. Of these 2817 reflections, 2254 had intensities greater than one estimated standard deviation. A reference reflection was measured hourly, and its intensity decreased gradually and smoothly with time. After a week of data collection, a diminution of 23% from the starting value had occurred. A check of the crystal orientation showed it to be unchanged, so the change in intensity is attributed to decomposition of the crystal by X-irradiation.

## Structure determination and refinement

The crystal specimen was a needle of about 0.057 cm length and about 0.017 cm diameter; its dimensions were carefully measured with the aid of a microscope. From these, transmission factors for  $\text{Mo-K}\alpha$  X-rays were calculated\*; they ranged from 0.65 to 0.74. By application of these factors, the

\* The computer programs used for this and the rest of this work and their accession numbers from the World List of Crystallographic Computer Programs [8] 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, a local version of A. Zalkin's FORDAP program by G. Brunton was used.

TABLE 1

POSITIONAL AND THERMAL PARAMETERS<sup>a</sup> AND THEIR STANDARD DEVIATIONS

Atom	x	y	z	$10^4 \beta_{11}$	$10^4 \beta_{22}$	$10^4 \beta_{33}$	$10^4 \beta_{12}$	$10^4 \beta_{13}$	$10^4 \beta_{23}$
Pr	-0.06611(6)	0.12753(3)	0.18311(5)	168.5(9)	29.9(2)	110.3(5)	-2.2(4)	43.8(5)	-6.2(3)
N	-0.3355(12)	0.1120(6)	-0.1213(9)	317(23)	73(5)	130(10)	39(9)	-17(13)	-18(7)
C(1)	0.1549(14)	0.1304(11)	0.0379(12)	300(25)	66(5)	189(17)	29(12)	141(17)	43(10)
C(2)	0.1858(20)	0.0771(8)	0.0995(21)	327(35)	55(6)	235(23)	-13(11)	130(23)	-53(11)
C(3)	0.2612(17)	0.0915(10)	0.2122(22)	187(29)	59(6)	362(36)	27(11)	129(26)	34(13)
C(4)	0.2662(16)	0.1568(10)	0.2226(15)	193(26)	100(9)	145(17)	-35(12)	52(16)	-17(10)
C(5)	0.2019(18)	0.1770(7)	0.1103(21)	325(33)	57(5)	281(28)	-72(11)	190(27)	-60(11)
C(6)	-0.0335(22)	0.0263(8)	0.3330(15)	519(49)	44(5)	176(18)	-26(12)	32(24)	23(7)
C(7)	-0.0785(22)	0.0004(5)	0.2262(17)	397(39)	28(3)	272(24)	1(10)	149(25)	16(7)
C(8)	-0.2368(22)	0.0159(6)	0.1723(11)	298(31)	39(4)	212(17)	-23(9)	73(21)	18(6)
C(9)	-0.3001(14)	0.0543(7)	0.2473(22)	146(22)	49(5)	355(31)	4(8)	116(22)	49(10)
C(10)	-0.1693(33)	0.0588(7)	0.3470(17)	657(61)	43(5)	231(24)	-1(14)	280(35)	23(8)
C(11)	-0.0786(34)	0.2537(9)	0.1961(38)	548(58)	35(4)	892(91)	-48(15)	577(70)	-71(18)
C(12)	-0.2184(40)	0.2416(9)	0.1207(22)	863(81)	44(6)	456(43)	85(18)	518(57)	58(12)
C(13)	-0.3199(15)	0.2124(7)	0.1673(22)	216(26)	45(4)	295(25)	34(8)	17(24)	-30(10)
C(14)	-0.2503(30)	0.2074(7)	0.2790(20)	489(53)	58(5)	203(23)	23(15)	156(28)	-29(10)
C(15)	-0.1038(34)	0.2343(10)	0.3062(18)	480(56)	69(8)	339(34)	56(17)	-65(34)	-116(14)
C(16)	-0.6022(13)	0.1384(5)	-0.2408(10)	272(23)	54(4)	186(14)	24(8)	68(16)	-4(7)
C(17)	-0.7246(15)	0.1381(6)	-0.3608(12)	349(29)	55(5)	170(15)	48(9)	-32(17)	-13(7)
C(18)	-0.6588(22)	0.1286(11)	-0.4497(14)	465(45)	191(14)	156(18)	81(22)	5(23)	-52(15)
C(19)	-0.5032(17)	0.0950(6)	-0.4435(10)	379(30)	80(5)	114(12)	39(10)	12(16)	-10(6)
C(20)	-0.3787(14)	0.0973(6)	-0.3255(11)	325(27)	74(5)	131(13)	19(9)	40(16)	-14(6)
C(21)	-0.4484(18)	0.1080(8)	-0.2331(11)	415(35)	116(9)	131(14)	115(15)	-48(19)	-36(9)
C(22)	-0.2503(14)	0.1139(5)	-0.0330(11)	327(28)	39(3)	161(14)	9(8)	40(16)	-2(6)

<sup>a</sup> Temperature factors are of the form:  $\exp(-h^2 \beta_{11} - k^2 \beta_{22} - l^2 \beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$ .

Lorentz and polarization factors, and by normalization to values interpolated between reference reflections, the intensity data were converted to structure factor squares,  $F_o^2$ , on a relative scale.

A Patterson function calculated with these data was readily interpreted to yield the positions of the Pr atoms; they occupy the fourfold general set of equipoints of space group  $P2_1/c$ . An electron-density map, calculated using phases determined by the Pr atoms alone, had peaks for each of the 22 C atoms and one N atom of the asymmetric unit; these atoms also occupy general positions of  $P2_1/c$ .

The approximate atomic positions thus obtained, anisotropic thermal parameters, and a scale factor were refined by the method of least squares using all observations with  $F_o > 1\sigma$ . The quantity minimized was  $\Sigma [1/\sigma^2(F_o^2) (F^2 - F_o^2)]^2$ , in which  $F$  is the calculated structure factor, properly scaled, and  $\sigma^2(F_o^2) = \sigma_c^2 + (0.03 F_o^2)^2$ ,  $\sigma_c^2$  being the variance due to counting statistics. In calculating  $F$ , the atomic scattering factors used for Pr, N and C were those of Cromer and Waber [9]; the Pr contribution was corrected for anomalous dispersion [10].

The H atoms were not discernible above the background in the electron-density maps. Their probable positions were calculated from the well known geometries of the cyclopentadienyl and cyclohexyl rings, and these positions along with isotropic thermal parameters were refined by least squares also. The result was a set of thermal B-values ranging from 5.2 to 22.4 and C—H bond lengths ranging from 0.8 to 1.2 Å. Clearly the H positions are not well determined, but we included their contributions in the final calculations because they have a noticeable influence on the positions adopted by the heavier atoms.

After convergence of the refinement,  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$  was 0.064 and the standard deviation of an observation of unit weight was 1.45. The refined positional and thermal parameters of all nonhydrogen atoms are listed in

TABLE 2  
INTERATOMIC DISTANCES IN Å

Bond	Length <sup>a</sup>	Bond	Length	Bond	Length
Pr—C(1)	2.83(1)	Pr—C(6)	2.80(1)	Pr—C(11)	2.74(2)
Pr—C(2)	2.76(1)	Pr—C(7)	2.81(1)	Pr—C(12)	2.79(2)
Pr—C(3)	2.76(1)	Pr—C(8)	2.79(1)	Pr—C(13)	2.76(1)
Pr—C(4)	2.75(1)	Pr—C(9)	2.76(1)	Pr—C(14)	2.75(2)
Pr—C(5)	2.80(1)	Pr—C(10)	2.77(1)	Pr—C(15)	2.80(1)
Pr—C(22)	2.65(1)	C(22)—N	1.11(1)	C(21)—N	1.42(2)
<i>Cyclopentadienyl rings</i>					
C(1)—C(2)	1.36(2)	C(6)—C(7)	1.35(2)	C(11)—C(12)	1.30(4)
C(2)—C(3)	1.37(2)	C(7)—C(8)	1.35(2)	C(12)—C(13)	1.29(2)
C(3)—C(4)	1.42(2)	C(8)—C(9)	1.42(2)	C(13)—C(14)	1.31(2)
C(4)—C(5)	1.38(2)	C(9)—C(10)	1.39(2)	C(14)—C(15)	1.31(2)
C(5)—C(1)	1.32(2)	C(10)—C(6)	1.37(2)	C(15)—C(11)	1.45(4)
<i>Cyclohexyl ring</i>					
C(16)—C(17)	1.53(2)	C(18)—C(19)	1.47(2)	C(20)—C(21)	1.39(2)
C(17)—C(18)	1.33(2)	C(19)—C(20)	1.52(2)	C(21)—C(16)	1.42(2)

<sup>a</sup> Numbers in parentheses are the standard deviations in the last significant digit.

TABLE 3  
MOLECULAR ANGLES

C Atom	Angle $^{\circ}$	C Atom	Angle	C Atom	Angle
1-2-3	108.3(1.5)	6-7-8	110.1(1.4)	11-12-13	111.4(2.5)
2-3-4	108.0(1.7)	7-8-9	108.6(1.3)	12-13-14	108.3(1.9)
3-4-5	103.7(1.6)	8-9-10	104.2(1.2)	13-14-15	110.6(1.9)
4-5-1	111.6(1.5)	9-10-6	110.1(1.5)	14-15-11	104.2(2.0)
5-1-2	108.2(1.4)	10-6-7	107.0(1.6)	15-11-12	105.0(1.7)
16-17-18	116.1(1.2)	18-19-20	114.2(1.1)	20-21-16	125.3(1.2)
17-18-19	125.0(1.5)	19-20-21	114.8(1.1)	21-16-17	115.3(1.0)
20-21-N	116.5(1.2)	21-N-22	177.8(1.7)		
16-21-N	113.3(1.1)	N-22-Pr	174.1(1.1)		

$^{\circ}$  Numbers in parentheses are the standard deviations in the last two digits of the value for the angle.

Table 1. A list of observed and calculated structure factors are available elsewhere \*. Interatomic distances and angles were calculated using the refined parameters, and relevant values are listed in Tables 2 and 3.

### Description and discussion of the structure

The structure consists of discrete  $(C_5H_5)_3Pr \cdot CNC_6H_{11}$  molecules packed as shown in Fig. 1. A closer look at one of these molecules is presented in Fig. 2. The coordination geometry of the Pr atom is that of a trigonal pyramid with the centroids of three cyclopentadienide rings forming the base and the C atom of the isonitrile molecule at its apex. The five-membered rings are planar within experimental error and their C-C bond lengths average 1.36 Å, which is about 0.03 Å smaller than usual for conjugated systems \*\*. These rings are  $\eta^5$ -bonded to the Pr atom, and the fifteen Pr-C distances range from 2.74 to 2.83 Å. This variation is probably of no chemical significance since the distances to the centroids of the rings are all identical (at 2.53 Å). The rings are quite symmetrically arrayed around the Pr atom, and the centroid-Pr-centroid angles average  $118.9^{\circ}$  with a range of  $\pm 0.1^{\circ}$ . The pyramidal arrangement in this molecule has been observed in two instances previously involving cyclopentadienide rings: tris(methylcyclopentadienide)neodymium(III) [7], in which the centroid-Nd-centroid angles average  $117.4 \pm 0.8^{\circ}$ , and tris(cyclopentadienyl)phenylethynyluranium(IV) [12], in which the corresponding angles average  $117 \pm 1.3^{\circ}$ . In these structures the nature and length of the carbon-metal bond at the apex varies widely: from a covalent  $\sigma$  bond in the uranium(IV) compound to the ionic attraction in the neodymium(III) compound.

\* The table of structure factors has been deposited as NAPS Document No. 02877 (10 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting \$5.00 for photocopies or \$3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

\*\* These bonds appear short because of the large thermal motions which the atoms are experiencing (rms displacements range up to 0.67 Å). Structures exhibiting this effect have been reported previously [11].

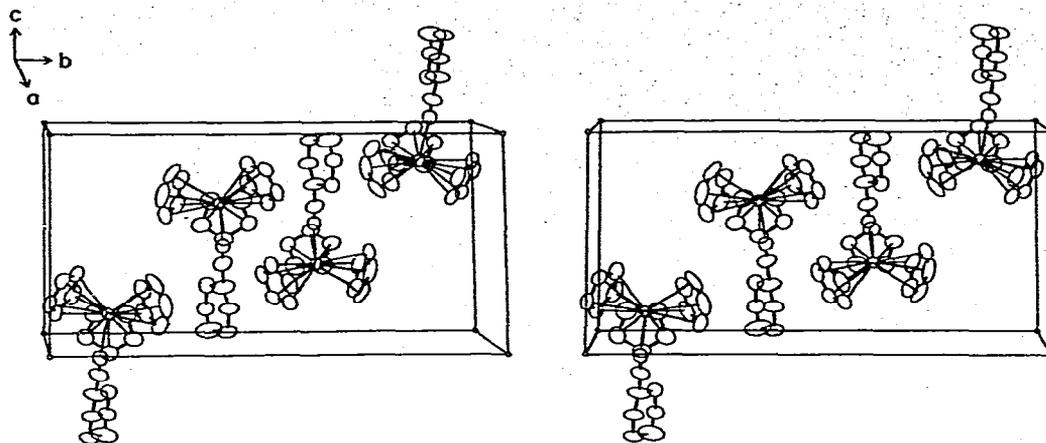


Fig. 1. Stereoscopic drawing of one unit cell of the structure of  $(C_5H_5)_3Pr \cdot CNC_6H_{11}$ .

Yet the geometry of the pyramid is the same in both these and in the present instance. Hence the factor determining these angles must be the closest packing of pentagonal rings within the coordination sphere. The need for a sixteenth C atom to complete the coordination was discussed previously [7] and is related to the size of the metal ion.

When the average  $\eta^5$ -bond length to the  $Pr^{3+}$  ion, 2.78 Å, in the present compound is compared with that to the  $Nd^{3+}$  ion in  $Nd(C_5H_4(CH_3))_3$  [7], 2.79 Å, and to the  $Sm^{3+}$  ion in  $Sm(C_9H_7)_3$  [13], 2.75 Å; the small differences

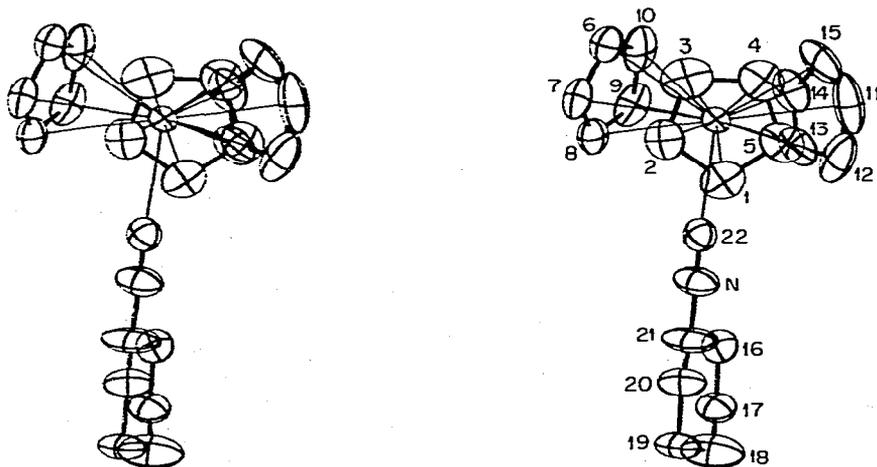


Fig. 2. Stereoscopic drawing of one molecule. Atoms are represented by their 50% probability thermal ellipsoids, and the numbers refer to C atoms.

can be accounted for by the differences in the lanthanide ionic radii, within experimental error. The  $\eta^1$ -bond length of 2.65Å from the Pr to the cyclohexylisonitrile molecule is 0.20Å longer than the Lu—C sigma bond in the  $[\text{Lu}(\text{C}_6\text{H}_3(\text{CH}_3)_2)_4]^-$  ion; this is due in part to a radius which is larger by 0.17Å and to the latter compound having only tetrahedral coordination [14].

The cyclohexyl ring is in the equatorial, chair form but is curiously flattened from the normal shape. This is obvious in Fig. 2 and is evidenced in the shortened bonds involving the atoms C(18) and C(21) at opposite ends of the chair and in the larger angles subtended at these atoms compared to those in the rest of the ring. These two atoms exhibit especially large thermal motions normal to the ring, and a possible alternative to the description of the ring as flattened can be offered, namely, that the ring is of normal chair shape, but disordered between two orientations differing by a 180° rotation about the (approximate) Pr—C—N axis. From the packing of molecules (Fig. 1), it appears that a ring in either orientation should fit in easily with the rest of the structure. Such a disordered model was refined by least squares but there is no significant difference in agreement indices between that model and the one with a single flattened ring as shown in Fig. 2.

From the increase in C≡N stretching frequency in this compound compared to that in the free isonitrile ligand, Fischer and Fischer [1] concluded that the C to Pr bond is of the  $\sigma$  donor type. The present work confirms this by showing a short Pr—C bond of length 2.65Å, a triple bond in the isonitrile with a C≡N length of 1.11Å, and a C≡N—C angle of 177.8(1.6)°. The geometry assumed by von Ammon, et al. [4] was found to be qualitatively correct, but the Pr—C≡N angle is 174.1(1.1)° which is a somewhat greater deviation from linearity than they expected. Of course, some deviation may result from packing in the solid and may not necessarily be the same as for the molecules in solution which were studied by NMR.

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