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Crystal Structure of the Dimer of Niobocene, $[(C_5H_5)(C_5H_4)NbH]_2$

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The structure of the μ-(*pentahapto*(*monohapto*)cyclopentadienyl)-(*pentahapto*cyclopentadienyl)hydridoniobium dimer was determined from X-ray counter data. The molecular structure has terminal hydrides and C_5H_5 ligands (pentahapto) and bridging C_5H_4 ligands (pentahapto and monohapto). Each dimer has idealized $C_2(2)$ molecular symmetry. The angle between the cyclopentadienyl rings in each monomer unit is 39.6 (4)°. Both types of cyclopentadienyl rings are planar with Nb–C(C_5H_5) distances of 2.398 (4) Å and Nb–C(C_5H_4) distances between 2.297 (3) and 2.439 (8) Å. The Nb–Nb distance is 3.105 (6) Å; each metal atom achieves an inert gas structure. The Nb–H distance is 1.70 (3) Å. The crystal structure consists of the packing of discrete dimeric molecules; three dimers are crystallographically unique. Crystals are orthorhombic, space group $P2_12_12_1$, with cell parameters of $a = 15.384$ (4), $b = 24.487$ (5), and $c = 12.879$ (3) Å. The structure was solved by Patterson superposition techniques and refined by least squares to a conventional R of 0.063.

Introduction

Since the discovery of ferrocene, bis(cyclopentadienyl)-metal complexes, metallocenes, have been prepared for many of the transition metal atoms. Structurally, the parent metallocenes are π-sandwich bonded as in ferrocene (parallel staggered rings) or ruthenocene (parallel eclipsed rings). The bis(cyclopentadienyl) complexes of niobium, tantalum, and titanium, however, do not have the simple π-bonded sandwich structure. They are dimeric metal hydrides. We report here the molecular and crystal structure of μ-(*pentahapto*-(*monohapto*)cyclopentadienyl)-(*pentahapto*cyclopentadienyl)hydridoniobium dimer (the dimer of niobocene), $[(C_5H_5)(C_5H_4)NbH]_2$. The tantalocene dimer is isomorphous with the niobocene dimer. A preliminary account of this work appeared earlier.[1]

In general the C_5H_5 ligand–metal bonding may be of the π-cyclopentadienyl, σ-cyclopentadienyl, or ionic cyclopentadienide type. The versatility of this ligand is illustrated in the dimer of niobocene by the bridging C_5H_4 ligand which is functionally both σ and π bonding (monohapto and pentahapto[2]) to different metal atoms. The bridging C_5H_4 geometry in $[(C_5H_5)(C_5H_4)NbH]_2$ is similar to that found in $(C_5H_5)(CO)Mo(C_5H_4)Mn(CO)_4$[3] and $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$;[4] the latter was reported to contain bridging C_5H_5 ligands, but the structural similarities with the niobocene dimer strongly support bridging C_5H_4 ligands.

Crystal Data and Structure Determination

The synthesis of $[(C_5H_5)(C_5H_4)NbH]_2$ was reported previously;[5] the pertinent spectral features are a Nb–H stretch at 1650 cm^{-1} in the infrared spectrum and nmr (H, 220 MHz) resonances at τ 12.07 (NbH), 5.11 (C_5H_5), 3.95 (one C_5H_4), and 5.6 (three C_5H_4).[5] Unsolvated orthorhombic and benzene-solvated triclinic crystals were grown.[1] The orthorhombic crystals were used in this study.

Crystals were enclosed in capillaries. The cell dimensions are $a = 15.384$ (4), $b = 24.487$ (5), and $c = 12.879$ (3) Å; these resulted from the least-squares refinement of the angular positions for 12 carefully centered reflections on the diffractometer. The diffraction extinctions of $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$) are characteristic of the space group $P2_12_12_1$. The observed and calculated densities for 12 dimers per cell are 1.85 and 1.83 g/cm^3, respectively. The implication for the space group $P2_12_12_1$ is that the crystallographically unique unit of this structure consists of six monomers, three dimers, or two trimers; we did not have a molecular weight at the beginning of this investigation. The crystal structure proved that there are three crystallographically unique dimers per cell. Subsequent molecular weight determinations showed the compound to be dimeric in solution also. All atoms are in general space group positions.[6]

The crystal used in the data collection was a platelet of dimensions 0.22 × 0.07 × 0.37 mm. The crystal was mounted on a Picker four-circle automatic diffractometer with the c^* axis coincident with the diffractometer ϕ axis. The data were measured with the θ–2θ scan technique using Zr-filtered Mo radiation (λ 0.7107 Å). Data were measured to 2θ of 45° with a scan range of 1.5° (1°/min) plus the Kα_1–Kα_2 separation. Backgrounds of 15 sec were measured before and after each scan. A total of 3340 reflections were measured.

The data were corrected for Lorentz, polarization, and absorption effects. The crystal was defined by six plane faces for the absorption correction. The linear absorption coefficient for Mo Kα radiation is 13.7 cm^{-1}. The maximum and minimum calculated transmission factors were 0.91 and 0.74, respectively. Structure factor errors were estimated as previously described;[7] data with F_o less than $3\sigma(F_o)$ were considered unobserved.

The structure solution was initiated using Patterson techniques (regular and sharpened[8]), but this was not straightforward because there are six niobium atoms in the asymmetric unit. The niobium atom positions were located using Patterson superposition techniques[9] in conjunction with the minimum function. Superposition vectors were taken from minor peaks in the Harker sections of the sharpened Patterson function. The R factor ($\Sigma \| F_o | - | F_c \| / \Sigma | F_o |$) based on the niobium atom positions only was 0.216. The remaining nonhydrogen atoms were found on an electron density difference map. The R was 0.075 with all nonhydrogen atoms in the model; the thermal parameters were anisotropic for the niobium atoms and isotropic for the other atoms.

An electron density difference map was examined for hydrogen atom positions. There were clear indications for most of the hydrogen atoms; however, the ring hydrogens were placed in calculated positions which were not refined. There were indications for the hydride hydrogen positions but only two of these could be unambiguously assigned (on Nb(3) and Nb(4)). These positions were included in the refinements with fixed isotropic thermal parameters of 4.0 Å^2.

The refinement continued with anisotropic thermal parameters for all nonhydrogen atoms. The refinements were done in three groups where each group was comprised of the positional and thermal parameters of one of the three crystallographically independent dimeric molecules. The final R and R_w ($[\Sigma w(|F_o| - |F_c|)^2/\Sigma w \cdot |F_o|^2]^{1/2}$) values for the 2620 observed reflections were 0.063 and 0.058, respectively. The final "error of fit," $(\Sigma w \| F_o | - | F_c \|^2/(m - n))^{1/2}$, was 1.068.

Each molecule is chiral and the crystals pack two molecules of enantiomer A for each molecule of enantiomer B (*vide infra*). The

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(3) R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 93, 536 (1971).

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(9) M. J. Buerger, "Vector Space," Wiley, New York, N. Y., 1959, p 252.

Table I. Positional Parameters for $[(C_5H_5)(C_5H_4)NbH]_2$ [a]

	x	y	z
Nb(1)	0.25908 (11)	0.01992 (7)	0.16016 (15)
Nb(2)	0.05675 (11)	0.02183 (7)	0.16839 (15)
Nb(3)	0.36794 (12)	0.34692 (8)	0.37341 (15)
Nb(4)	0.46187 (12)	0.26671 (7)	0.52156 (15)
Nb(5)	0.31954 (11)	0.60687 (8)	0.35645 (14)
Nb(6)	0.33355 (13)	0.71784 (8)	0.47159 (16)
C(1)	0.1570 (14)	0.0797 (8)	0.2220 (16)
C(2)	0.2125 (14)	0.1106 (8)	0.1590 (18)
C(3)	0.2960 (15)	0.1151 (8)	0.1963 (21)
C(4)	0.3015 (14)	0.0868 (9)	0.2883 (20)
C(5)	0.2155 (14)	0.0655 (9)	0.3119 (17)
C(6)	0.1564 (12)	0.0097 (7)	0.0368 (14)
C(7)	0.1011 (12)	0.0526 (8)	0.0095 (15)
C(8)	0.0173 (15)	0.0332 (9)	−0.0117 (16)
C(9)	0.0135 (14)	−0.0219 (9)	0.0039 (15)
C(10)	0.1010 (14)	−0.0381 (8)	0.0367 (16)
C(11)	0.2475 (12)	−0.0738 (8)	0.2005 (16)
C(12)	0.2956 (16)	−0.0720 (9)	0.1051 (18)
C(13)	0.3708 (16)	−0.0442 (9)	0.1291 (20)
C(14)	0.3737 (16)	−0.0334 (9)	0.2363 (19)
C(15)	0.2965 (15)	−0.0513 (9)	0.2823 (18)
C(16)	0.0612 (14)	−0.0279 (9)	0.3302 (15)
C(17)	0.0168 (14)	0.0241 (9)	0.3522 (14)
C(18)	−0.0589 (14)	0.0217 (9)	0.2939 (15)
C(19)	−0.0656 (15)	−0.0267 (11)	0.2359 (20)
C(20)	0.0123 (15)	−0.0577 (8)	0.2604 (15)
C(21)	0.4655 (13)	0.2772 (8)	0.3497 (15)
C(22)	0.5050 (13)	0.3257 (8)	0.3023 (15)
C(23)	0.4537 (15)	0.3403 (9)	0.2117 (16)
C(24)	0.3863 (13)	0.3058 (10)	0.2003 (17)
C(25)	0.3947 (15)	0.2669 (8)	0.2798 (17)
C(26)	0.4424 (13)	0.3600 (7)	0.5204 (16)
C(27)	0.5336 (12)	0.3501 (8)	0.5279 (17)
C(28)	0.5539 (15)	0.3241 (9)	0.6259 (18)
C(29)	0.4790 (16)	0.3210 (8)	0.6772 (14)
C(30)	0.4074 (13)	0.3407 (8)	0.6172 (16)
C(31)	0.2369 (14)	0.3314 (10)	0.4704 (21)
C(32)	0.2547 (13)	0.3890 (9)	0.4782 (20)
C(33)	0.2493 (14)	0.4106 (9)	0.3753 (19)
C(34)	0.2257 (14)	0.3675 (11)	0.3093 (18)
C(35)	0.2197 (14)	0.3204 (10)	0.3641 (20)
C(36)	0.3423 (15)	0.2025 (8)	0.5015 (18)
C(37)	0.4176 (16)	0.1773 (8)	0.4679 (19)
C(38)	0.4745 (16)	0.1706 (9)	0.5512 (23)
C(39)	0.4334 (17)	0.1956 (10)	0.6422 (16)
C(40)	0.3507 (17)	0.2152 (9)	0.6066 (19)
C(41)	0.2818 (12)	0.6357 (8)	0.5194 (14)
C(42)	0.2080 (12)	0.6105 (10)	0.4769 (16)
C(43)	0.2211 (13)	0.5544 (8)	0.4634 (18)
C(44)	0.3026 (14)	0.5405 (8)	0.5013 (18)
C(45)	0.3419 (14)	0.5895 (8)	0.5327 (16)
C(46)	0.2752 (13)	0.6899 (9)	0.3155 (16)
C(47)	0.2081 (14)	0.7213 (10)	0.3698 (15)
C(48)	0.2270 (15)	0.7764 (9)	0.3839 (18)
C(49)	0.3061 (14)	0.7833 (10)	0.3342 (21)
C(50)	0.3348 (14)	0.7341 (9)	0.2914 (15)
C(51)	0.4582 (14)	0.6261 (11)	0.2799 (21)
C(52)	0.4008 (15)	0.6157 (10)	0.1988 (18)
C(53)	0.3727 (12)	0.5641 (9)	0.2002 (16)
C(54)	0.4140 (13)	0.5400 (7)	0.2864 (17)
C(55)	0.4673 (13)	0.5778 (9)	0.3352 (18)
C(56)	0.4777 (12)	0.6916 (9)	0.5243 (19)
C(57)	0.4322 (15)	0.7006 (11)	0.6146 (20)
C(58)	0.4091 (14)	0.7564 (12)	0.6166 (17)
C(59)	0.4453 (17)	0.7776 (10)	0.5273 (22)
C(60)	0.4872 (16)	0.7386 (9)	0.4650 (17)

[a] The standard deviations of the least significant digits are given in parentheses.

question arises whether the packing is A,A,B or B,B,A. To investigate this, the crystal was remounted and 54 Bijvoet pairs were examined for those reflections which gave the largest differences in calculated structure factors for hkl and $\bar{h}\bar{k}\bar{l}$. The observed differences were small, on the order of 1σ or less, but the net result confirmed the distribution reported here. There were 37 positive indications and 13 negative indications, and 4 comparisons showed no preference.

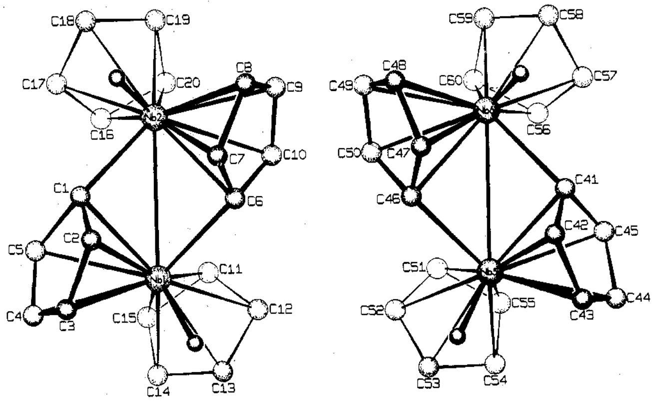

Figure 1. The molecular structure of $[(C_5H_5)(C_5H_4)NbH]_2$. Two of the unique molecules have the left conformation while the third is the enantiomorph on the right.

Neutral atom form factors were used.[10] The niobium atom was corrected for the real and imaginary parts of the anomalous scattering effect[11] in the calculated structure factors. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the least-squares refinement.[12]

The final refined positional parameters are given in Table I and thermal parameters in Table II. The hydrogen atom positions are given in Table III; the hydrogens are identified also by the atoms to which they are attached. A list of observed and calculated structure factors (×5) is available.[13]

Structure Description

The crystal structure consists of the packing of discrete dimeric molecules. The molecular structure is illustrated in Figure 1. Two of the crystallographically unique molecules are like that on the left and the third is the enantiomorph shown on the right of Figure 1. It is clear from these accurately drawn atomic positions that the molecules are enantiomorphs (vertical mirror plane). The numbering system chosen has atoms Nb(1), Nb(2), C(1)-C(20) in molecule one, Nb(3), Nb(4), C(21)-C(40) in molecule two, and Nb(5), Nb(6), C(41)-C(60) in molecule three. The carbon atoms in molecules two and three, chemically equivalent to those in molecule one, are identified by adding 20 and 40, respectively, to the atom numbers in molecule one. Each molecule has $C_2(2)$ idealized molecular symmetry. The $C_2(2)$ axis in Figure 1 is through the center of the molecule, normal to the plane of the paper.

Each dimer contains terminal cyclopentadienyl ligands and hydride hydrogens, bridging C_5H_4 ligands, and an Nb-Nb bond. A selected set of interatomic distances is given in Table IV listed according to type and in columns according to chemical equivalence in the three unique molecules. The distances were not corrected for thermal motion. A selected set of interatomic angles is given in Table V. Inspection of Tables IV and V shows that the distances and angles for the three molecules do not differ significantly from the mean in

(10) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(11) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 216.

(12) Computer programs used in addition to local programs were Prewitt's absorption correction program ACACA and least-squares program SFLS5, the Busing-Levy error function program ORFFE, the Johnson plotting program ORTEP, and the Fourier program FOUR, a modification of a program wirtten by C. J. Fritchie, Jr.

(13) A list of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth 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-73-294.

Table II. Thermal Parameters (× 10^4) for $[(C_5H_5)(C_5H_4)NbH]_2$[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb(1)	26.5 (9)	10.4 (4)	43.8 (15)	0.3 (5)	−1.7 (10)	−2.7 (7)
Nb(2)	24.8 (9)	9.5 (4)	36.3 (14)	−0.1 (5)	1.7 (10)	−2.3 (7)
Nb(3)	28.6 (9)	11.0 (4)	44.8 (15)	2.2 (5)	−1.2 (10)	−1.7 (7)
Nb(4)	29.4 (9)	8.2 (4)	40.9 (14)	−1.6 (5)	−4.7 (10)	1.1 (6)
Nb(5)	23.2 (9)	14.9 (4)	37.2 (14)	1.1 (5)	−0.6 (10)	1.3 (7)
Nb(6)	30.9 (10)	14.2 (4)	49.5 (15)	−0.7 (6)	0.0 (12)	1.9 (7)
C(1)	30 (11)	8 (4)	63 (17)	−7 (6)	9 (13)	3 (7)
C(2)	37 (11)	10 (4)	79 (20)	−2 (6)	−25 (14)	−3 (8)
C(3)	60 (15)	1 (4)	113 (25)	−2 (6)	−3 (16)	−3 (8)
C(4)	27 (12)	10 (5)	114 (23)	0 (6)	−26 (14)	−26 (9)
C(5)	36 (11)	13 (5)	60 (18)	3 (6)	10 (12)	−5 (8)
C(6)	52 (11)	14 (4)	15 (12)	17 (6)	7 (11)	−2 (6)
C(7)	34 (10)	9 (4)	23 (14)	1 (5)	−3 (10)	6 (7)
C(8)	61 (15)	10 (5)	32 (16)	11 (6)	−31 (13)	−12 (7)
C(9)	49 (13)	15 (5)	46 (16)	−2 (7)	−3 (12)	−17 (8)
C(10)	49 (13)	11 (5)	33 (15)	−1 (6)	0 (12)	−2 (7)
C(11)	20 (10)	8 (4)	36 (16)	−3 (5)	5 (12)	8 (7)
C(12)	32 (13)	10 (5)	92 (21)	3 (7)	−22 (14)	−10 (8)
C(13)	62 (14)	12 (5)	64 (22)	3 (7)	16 (16)	−3 (9)
C(14)	45 (14)	11 (5)	62 (20)	6 (7)	0 (14)	4 (8)
C(15)	41 (12)	15 (5)	66 (20)	10 (7)	−13 (14)	0 (9)
C(16)	48 (12)	15 (5)	18 (13)	2 (7)	28 (12)	6 (7)
C(17)	61 (12)	18 (5)	7 (14)	−2 (7)	4 (12)	−6 (8)
C(18)	39 (11)	23 (5)	15 (14)	−12 (7)	−5 (11)	8 (8)
C(19)	24 (12)	34 (7)	94 (22)	−19 (8)	11 (14)	8 (11)
C(20)	52 (13)	12 (5)	22 (15)	−8 (6)	9 (11)	3 (7)
C(21)	46 (11)	10 (4)	34 (16)	3 (6)	14 (12)	−1 (7)
C(22)	46 (12)	13 (5)	16 (14)	2 (6)	−2 (11)	−14 (7)
C(23)	58 (14)	16 (5)	32 (15)	−1 (8)	34 (13)	12 (7)
C(24)	26 (11)	25 (6)	46 (18)	4 (7)	11 (12)	2 (8)
C(25)	57 (14)	10 (4)	40 (18)	−4 (6)	3 (14)	−1 (8)
C(26)	29 (11)	5 (3)	44 (16)	−6 (5)	0 (12)	−9 (6)
C(27)	26 (10)	14 (4)	53 (17)	−12 (6)	12 (12)	−9 (8)
C(28)	51 (13)	17 (5)	48 (19)	1 (7)	11 (15)	−10 (8)
C(29)	78 (15)	15 (5)	6 (14)	4 (7)	7 (13)	−4 (7)
C(30)	53 (12)	11 (4)	30 (15)	1 (6)	−20 (12)	−6 (7)
C(31)	33 (12)	19 (5)	94 (23)	−3 (7)	−16 (15)	3 (10)
C(32)	16 (10)	18 (5)	104 (23)	6 (6)	30 (14)	−9 (10)
C(33)	41 (12)	14 (5)	78 (20)	8 (6)	23 (14)	6 (9)
C(34)	33 (12)	23 (6)	67 (20)	15 (7)	−9 (13)	−3 (10)
C(35)	41 (13)	22 (6)	75 (22)	−5 (7)	−16 (15)	1 (10)
C(36)	48 (13)	10 (4)	78 (21)	−2 (7)	−7 (14)	8 (8)
C(37)	64 (15)	4 (4)	63 (19)	−9 (6)	−9 (15)	14 (7)
C(38)	67 (16)	13 (5)	101 (26)	−4 (7)	−21 (18)	−7 (10)
C(39)	82 (16)	18 (6)	22 (16)	−17 (8)	−24 (15)	4 (8)
C(40)	74 (17)	11 (5)	54 (20)	−9 (8)	8 (16)	1 (8)
C(41)	32 (10)	16 (5)	20 (14)	−4 (6)	−4 (10)	9 (7)
C(42)	18 (10)	26 (6)	42 (16)	−2 (6)	18 (11)	5 (9)
C(43)	36 (12)	12 (5)	68 (18)	−4 (6)	30 (13)	−1 (8)
C(44)	35 (12)	11 (4)	80 (22)	6 (6)	12 (13)	8 (8)
C(45)	54 (12)	7 (4)	50 (16)	−4 (6)	18 (14)	7 (7)
C(46)	28 (10)	18 (5)	41 (17)	−6 (6)	2 (11)	−1 (8)
C(47)	47 (13)	27 (6)	25 (15)	2 (7)	−7 (12)	11 (8)
C(48)	43 (13)	10 (5)	89 (21)	1 (6)	−4 (14)	0 (8)
C(49)	34 (12)	26 (7)	101 (24)	−1 (7)	−15 (15)	−7 (12)
C(50)	48 (13)	19 (5)	34 (14)	5 (8)	22 (12)	9 (7)
C(51)	30 (12)	24 (7)	103 (23)	−3 (8)	10 (15)	−11 (11)
C(52)	45 (14)	19 (6)	62 (19)	−3 (7)	24 (14)	−7 (9)
C(53)	16 (9)	12 (5)	68 (18)	9 (6)	−12 (11)	−13 (8)
C(54)	32 (11)	5 (4)	62 (17)	3 (5)	35 (12)	4 (7)
C(55)	27 (11)	16 (5)	87 (20)	7 (6)	−13 (14)	−10 (10)
C(56)	19 (11)	25 (6)	52 (18)	−4 (6)	3 (12)	5 (9)
C(57)	41 (13)	24 (7)	73 (23)	−3 (8)	−27 (15)	−8 (10)
C(58)	40 (12)	33 (7)	32 (17)	3 (8)	−18 (12)	−24 (10)
C(59)	84 (17)	19 (6)	72 (22)	−5 (8)	−15 (18)	−8 (11)
C(60)	78 (16)	16 (5)	45 (18)	−14 (8)	18 (15)	−7 (9)

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

view of the errors involved. Also, the molecules do not show significant deviations from the idealized $C_2(2)$ symmetry. The geometry averaged over the six unique monomeric units (three dimers) is given in Table VI.

The Nb-Nb bond length of 3.105 (6) Å is in the range of frequently observed metal-metal bond lengths and may be compared with the Nb-Nb distances of 3.31 Å in α-NbI_4,[14] 2.85 Å in $[Nb_6Cl_{12}]^{2+}$,[15] 2.86 Å in niobium metal,[16] and

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Table III. Hydrogen Atom Positions for $[(C_5H_5)(C_5H_4)NbH]_2$

	x	*y*	*z*
H(1)Nb(3)	0.3767 (116)	0.4095 (75)	0.3101 (146)
H(2)Nb(4)	0.5644 (119)	0.2489 (78)	0.4976 (155)
H(3)C(2)	0.1925	0.1274	0.0936
H(4)C(3)	0.3441	0.1365	0.1646
H(5)C(4)	0.3552	0.0819	0.3331
H(6)C(5)	0.1994	0.0449	0.3788
H(7)C(7)	0.1198	0.0923	0.0069
H(8)C(8)	−0.0315	0.0569	−0.0357
H(9)C(9)	−0.0389	−0.0459	−0.0035
H(10)C(10)	0.1188	−0.0759	0.0557
H(11)C(11)	0.1881	−0.0899	0.2096
H(12)C(12)	0.2783	−0.0868	0.0356
H(13)C(13)	0.4178	−0.0335	0.0776
H(14)C(14)	0.4227	−0.0144	0.2760
H(15)C(15)	0.2798	−0.0493	0.3563
H(16)C(16)	0.1176	−0.0397	0.3613
H(17)C(17)	0.0369	0.0545	0.3994
H(18)C(18)	−0.1040	0.0507	0.2919
H(19)C(19)	−0.1130	−0.0379	0.1862
H(20)C(20)	0.0285	−0.0942	0.2328
H(21)C(22)	0.5576	0.3462	0.3284
H(22)C(23)	0.4658	0.3720	0.1657
H(23)C(24)	0.3403	0.3057	0.1431
H(24)C(25)	0.3534	0.2356	0.2941
H(25)C(27)	0.5768	0.3595	0.4714
H(26)C(28)	0.6117	0.3113	0.6496
H(27)C(29)	0.4735	0.3075	0.7507
H(28)C(30)	0.3446	0.3395	0.6381
H(29)C(31)	0.2382	0.3038	0.5292
H(30)C(32)	0.2669	0.4098	0.5441
H(31)C(33)	0.2593	0.4492	0.3534
H(32)C(34)	0.2149	0.3714	0.2326
H(33)C(35)	0.2054	0.2843	0.3336
H(34)C(36)	0.2904	0.2106	0.4568
H(35)C(37)	0.4303	0.1649	0.3963
H(36)C(38)	0.5335	0.1520	0.5522
H(37)C(39)	0.4561	0.1987	0.7121
H(38)C(40)	0.3069	0.2356	0.6490
H(39)C(42)	0.1524	0.6300	0.4588
H(40)C(43)	0.1787	0.5285	0.4304
H(41)C(44)	0.3280	0.5028	0.5047
H(42)C(45)	0.4023	0.5920	0.5612
H(43)C(47)	0.1531	0.7050	0.3965
H(44)C(48)	0.1920	0.8047	0.4213
H(45)C(49)	0.3381	0.8188	0.3291
H(46)C(50)	0.3908	0.7297	0.2516
H(47)C(51)	0.4877	0.6617	0.2960
H(48)C(52)	0.3834	0.6441	0.1464
H(49)C(53)	0.3319	0.5468	0.1514
H(50)C(54)	0.4062	0.5012	0.3096
H(51)C(55)	0.5050	0.5714	0.3983
H(52)C(56)	0.5019	0.6552	0.5028
H(53)C(57)	0.4187	0.6716	0.6679
H(54)C(58)	0.3746	0.7748	0.6714
H(55)C(59)	0.4412	0.8171	0.5099
H(56)C(60)	0.5166	0.7439	0.3961

2.74 Å in $[(C_5H_5)Nb(CO)[(C_6H_5)_2C_2]]_2$.[17] Double-bond character is postulated in the latter structure. An Nb-Nb single bond distance of 3.20 Å is calculated using the niobium radius derived from the Nb-C(C_5H_5) distance (2.40-0.80 Å).[18] Metal-metal distances with similar bridging geometries are 2.961 Å for Mo-Mn with a single-bridging C_5H_4 in $(C_5H_5)(CO)Mo(C_5H_4)Mn(CO)_4$[3] and 3.105 (5) Å for Ti-Ti in $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$.[4] The Nb-Nb bond length is not a good criterion for bond order here because it may be affected by the constraints of the bridging geometry.

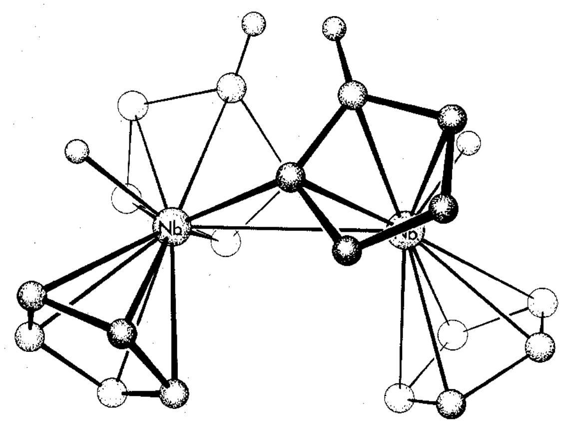

Figure 2. The molecular structure of $[(C_5H_5)(C_5H_4)NbH]_2$ with the idealized C_2 (2) axis vertical. The two bridging C_5H_4 ring hydrogens in close contact are shown.

The average Nb-C(C_5H_5) distance of 2.398 (4) Å compares with 2.44 Å in $(C_5H_5)Nb(CO)[(C_6H_5)_4C_4][(C_6H_5)_2C_2]$,[19] 2.45 Å in $[(C_5H_5)Nb(CO)[(C_6H_5)_2C_2]]_2$,[17] and 2.46 Å in $(C_5H_5)Nb(CO)[(C_6H_5)_2C_2]_2$.[20] The C-C distances in both types of cyclopentadienyl ligands are in the range of values frequently found for cyclopentadienyl ligands.[21]

The Nb-H distance of 1.70 (3) Å is in the range of observed metal-hydride distances.[22] Although only two of the six hydride hydrogens were located, they establish the hydride geometry for molecule two; the molecular geometries of molecules one and three are clearly the same in view of the similar distances and angles (Tables IV and V).

The least-squares planes for the cyclopentadienyl rings are given in Table VII along with some pertinent dihedral angles. The C_5H_4 rings are not noticeably less planar than the C_5H_5 rings.

Discussion

The most unusual structural feature is the bridging C_5H_4 ligands. The planar C_5H_4 ligands are tilted (2.439 (8) Å for Nb(1)-C(3) to 2.297 (3) Å for Nb(1)-C(1), Table VI) enabling them to σ bond to the second niobium atom. The σ bond of 2.232 (7) Å is bent 31.6° out of the C_5H_4 plane toward the second niobium atom; the short length and large angle here indicate nonlinear orbital overlap (bent bonds). The angle between the two planes formed by the bridging carbon atoms and the niobium atoms is 49.3° (130.7° between normals). This is evident when Figure 2 is compared with Figure 1. In Figure 2 the molecular $C_2(2)$ axis is vertical.

The average of the C-C distances in the C_5H_4 ligand (Table VI) is 1.418 (7) Å; however, the data indicate they can be separated into one short (1.368 (10) Å for C(3)-C(4)), two intermediate (1.418 (9) Å for C(2)-C(3)), and two long (1.443 (10) Å for C(1)-C(2)). In a purely statistical sense the differences are surely significant if the estimated errors are meaningful. They also correlate in a chemical sense with

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Table IV. Interatomic Distances (Å) for $[(C_5H_5)(C_5H_4)NbH]_2$

Molecule 1		Molecule 2		Molecule 3	
Atoms	Dist	Atoms	Dist	Atoms	Dist
Nb(1)-Nb(2)	3.115 (3)	Nb(3)-Nb(4)	3.096 (3)	Nb(5)-Nb(6)	3.103 (3)
Nb(1)–C(6)	2.25 (2)	Nb(3)–C(26)	2.24 (2)	Nb(5)–C(46)	2.21 (2)
Nb(2)–C(1)	2.21 (2)	Nb(4)–C(21)	2.23 (2)	Nb(6)–C(41)	2.25 (2)
		Nb(3)-H(1)	1.74 (18)		
		Nb(4)-H(2)	1.67 (18)		
		$Nb–C(C_5H_4)$			
Nb(1)–C(1)	2.29 (2)	Nb(3)–C(21)	2.29 (2)	Nb(5)–C(41)	2.29 (2)
Nb(1)–C(2)	2.33 (2)	Nb(3)–C(22)	2.36 (2)	Nb(5)–C(42)	2.31 (2)
Nb(1)–C(3)	2.44 (2)	Nb(3)–C(23)	2.47 (2)	Nb(5)–C(43)	2.42 (2)
Nb(1)–C(4)	2.41 (2)	Nb(3)–C(24)	2.46 (2)	Nb(4)–C(44)	2.49 (2)
Nb(1)–C(5)	2.35 (2)	Nb(3)–C(25)	2.34 (2)	Nb(5)–C(45)	2.33 (2)
Nb(2)–C(6)	2.30 (3)	Nb(4)–C(26)	2.30 (2)	Nb(6)–C(46)	2.31 (2)
Nb(2)–C(7)	2.28 (2)	Nb(4)–C(27)	2.32 (2)	Nb(6)–C(47)	2.33 (2)
Nb(2)–C(8)	2.41 (2)	Nb(4)–C(28)	2.41 (2)	Nb(6)–C(48)	2.45 (2)
Nb(2)–C(9)	2.47 (2)	Nb(4)–C(29)	2.42 (2)	Nb(6)–C(49)	2.42 (2)
Nb(2)–C(10)	2.34 (2)	Nb(4)–C(30)	2.35 (2)	Nb(6)–C(50)	2.35 (2)
		$Nb–C(C_5H_5)$			
Nb(1)–C(11)	2.36 (2)	Nb(3)–C(31)	2.40 (2)	Nb(5)–C(51)	2.40 (2)
Nb(1)–C(12)	2.43 (2)	Nb(3)–C(32)	2.43 (2)	Nb(5)–C(52)	2.39 (2)
Nb(1)–C(13)	2.36 (2)	Nb(3)–C(33)	2.40 (2)	Nb(5)–C(53)	2.41 (2)
Nb(1)–C(14)	2.40 (2)	Nb(3)–C(34)	2.39 (2)	Nb(5)–C(54)	2.37 (2)
Nb(1)–C(15)	2.42 (2)	Nb(3)–C(35)	2.37 (2)	Nb(5)–C(55)	2.40 (2)
Nb(2)–C(16)	2.41 (2)	Nb(4)–C(35)	2.43 (2)	Nb(6)–C(56)	2.41 (2)
Nb(2)–C(17)	2.45 (2)	Nb(4)–C(37)	2.39 (2)	Nb(6)–C(57)	2.42 (2)
Nb(2)–C(18)	2.40 (2)	Nb(4)–C(38)	2.39 (2)	Nb(6)–C(58)	2.39 (2)
Nb(2)–C(19)	2.39 (2)	Nb(4)–C(39)	2.38 (2)	Nb(6)–C(59)	2.37 (2)
Nb(2)–C(20)	2.38 (2)	Nb(4)–C(40)	2.39 (2)	Nb(6)–C(60)	2.42 (2)
		$C–C(C_5H_4)$			
C(1)–C(2)	1.40 (3)	C(21)–C(22)	1.47 (3)	C(41)–C(42)	1.40 (2)
C(2)–C(3)	1.38 (3)	C(22)–C(23)	1.45 (3)	C(42)–C(43)	1.40 (3)
C(3)–C(4)	1.38 (3)	C(23)–C(24)	1.35 (3)	C(43)–C(44)	1.39 (3)
C(4)–C(5)	1.45 (3)	C(24)–C(25)	1.40 (3)	C(44)–C(45)	1.40 (3)
C(5)–C(1)	1.51 (3)	C(25)–C(21)	1.44 (3)	C(45)–C(41)	1.47 (3)
C(6)–C(7)	1.40 (2)	C(26)–C(27)	1.43 (2)	C(46)–C(47)	1.46 (3)
C(7)–C(8)	1.40 (3)	C(27)–C(28)	1.45 (3)	C(47)–C(48)	1.39 (3)
C(8)–C(9)	1.37 (3)	C(28)–C(39)	1.33 (3)	C(48)–C(49)	1.39 (3)
C(9)–C(10)	1.47 (3)	C(29)–C(30)	1.43 (3)	C(49)–C(50)	1.40 (3)
C(10)–C(6)	1.45 (3)	C(30)–C(26)	1.44 (3)	C(50)–C(46)	1.45 (3)
		$C–C(C_5H_5)$			
C(11)–C(12)	1.43 (3)	C(31)–C(32)	1.44 (3)	C(51)–C(52)	1.39 (3)
C(12)–C(13)	1.38 (3)	C(32)–C(33)	1.43 (3)	C(52)–C(53)	1.34 (3)
C(13)–C(14)	1.41 (3)	C(33)–C(34)	1.40 (3)	C(53)–C(54)	1.41 (3)
C(14)–C(15)	1.40 (3)	C(34)–C(35)	1.35 (3)	C(54)–C(55)	1.39 (3)
C(15)–C(11)	1.41 (3)	C(35)–C(31)	1.42 (3)	C(55)–C(51)	1.39 (3)
C(16)–C(17)	1.47 (3)	C(36)–C(37)	1.38 (3)	C(56)–C(57)	1.38 (3)
C(17)–C(18)	1.39 (3)	C(37)–C(38)	1.39 (3)	C(57)–C(58)	1.41 (3)
C(18)–C(19)	1.40 (3)	C(38)–C(39)	1.47 (3)	C(58)–C(59)	1.38 (3)
C(19)–C(20)	1.45 (3)	C(39)–C(40)	1.43 (3)	C(59)–C(60)	1.40 (3)
C(20)–C(16)	1.38 (3)	C(40)–C(36)	1.39 (3)	C(60)–C(56)	1.39 (3)
		Nonbonding			
Nb(1)–C(7)	3.21 (2)	Nb(3)–C(27)	3.23 (2)	Nb(5)–C(47)	3.29 (2)
Nb(1)–C(10)	3.23 (2)	Nb(3)–C(30)	3.20 (2)	Nb(5)–C(50)	3.23 (2)
Nb(2)–C(2)	3.24 (2)	Nb(4)–C(22)	3.24 (2)	Nb(6)–C(42)	3.26 (2)
Nb(2)–C(5)	3.24 (2)	Nb(4)–C(25)	3.28 (2)	Nb(6)–C(45)	3.24 (2)
C(1)–C(6)	2.94 (3)	C(21)–C(26)	3.01 (3)	C(41)–C(46)	2.94 (3)
C(1)–C(7)	2.95 (3)	C(21)–C(27)	3.09 (3)	C(41)–C(47)	3.06 (3)
C(1)–C(17)	3.05 (3)	C(21)–C(37)	2.97 (3)	C(41)–C(57)	3.06 (3)
C(2)–C(6)	3.05 (3)	C(22)–C(26)	3.09 (3)	C(42)–C(46)	3.03 (3)
C(2)–C(7)	2.94 (3)	C(22)–C(27)	3.00 (3)	C(42)–C(47)	3.04 (3)
C(6)–C(12)	3.06 (3)	C(26)–C(32)	3.02 (3)	C(46)–C(52)	3.05 (3)

the bonding of the bridging ring and the observed variation in Nb-$C(C_5H_4)$ distances. The bridging carbon atom, C(1), is not displaced significantly out of the C_5H_4 plane as judged by the dihedral angle between the C(1)C(2)C(5) and C(2)C(3)-C(4)C(5) planes; the maximum observed dihedral angle is 3.7°. For the six C_5H_4 ligands, three of the bridging carbon atoms are displaced toward the niobium atoms and three are displaced the other way. A single dihedral angle of 4° was found in $(C_5H_5)(CO)Mo(C_5H_4)Mn(CO)_4$.[3] There do not appear to be any systematic variations in the C-$C(C_5H_5)$ distances.

Initially we thought the C-$C(C_5H_4)$ bond distances would reveal one quite distinct carbon atom since the four bridging hydrogens split in the nmr with one hydrogen about 1.7 ppm

Table V. Interatomic Angles (Deg) for $[(C_5H_5)(C_5H_4)NbH]_2$

Molecule 1		Molecule 2		Molecule 3	
Atoms	Angle	Atoms	Angle	Atoms	Angle
Nb(2)-Nb(1)-C(1)	45.0 (5)	Nb(4)-Nb(3)-C(21)	45.9 (5)	Nb(6)-Nb(5)-C(41)	46.3 (5)
Nb(2)-Nb(1)-C(6)	47.6 (4)	Nb(4)-Nb(3)-C(26)	48.0 (4)	Nb(6)-Nb(5)-C(46)	47.9 (5)
Nb(1)-Nb(2)-C(1)	47.3 (5)	Nb(3)-Nb(4)-C(21)	47.7 (5)	Nb(5)-Nb(6)-C(41)	47.4 (5)
Nb(1)-Nb(2)-C(6)	46.2 (5)	Nb(3)-Nb(4)-C(26)	46.1 (5)	Nb(5)-Nb(6)-C(46)	45.3 (5)
Nb(1)-C(1)-Nb(2)	87.7 (7)	Nb(3)-C(21)-Nb(4)	86.4 (6)	Nb(5)-C(41)-Nb(6)	86.3 (6)
Nb(4)-C(6)-Nb(2)	86.2 (6)	Nb(3)-C(26)-Nb(4)	86.0 (6)	Nb(5)-C(46)-Nb(6)	86.8 (7)
		C-Nb-C(C_5H_4)			
C(1)-Nb(1)-C(2)	35.2 (6)	C(21)-Nb(3)-C(22)	36.7 (6)	C(41)-Nb(5)-C(42)	35.5 (6)
C(2)-Nb(1)-C(3)	33.4 (6)	C(22)-Nb(3)-C(23)	34.9 (6)	C(42)-Nb(5)-C(43)	34.3 (6)
C(3)-Nb(1)-C(4)	32.9 (7)	C(23)-Nb(3)-C(24)	31.7 (7)	C(43)-Nb(5)-C(44)	32.9 (6)
C(4)-Nb(1)-C(5)	35.5 (7)	C(24)-Nb(3)-C(25)	33.9 (7)	C(44)-Nb(5)-C(45)	33.7 (6)
C(5)-Nb(1)-C(1)	37.9 (7)	C(25)-Nb(3)-C(21)	36.1 (7)	C(45)-Nb(5)-C(41)	37.1 (6)
C(6)-Nb(2)-C(7)	35.4 (6)	C(26)-Nb(4)-C(27)	35.9 (6)	C(46)-Nb(6)-C(47)	36.8 (7)
C(7)-Nb(2)-C(8)	34.5 (7)	C(27)-Nb(4)-C(28)	35.6 (7)	C(47)-Nb(6)-C(48)	33.7 (7)
C(8)-Nb(2)-C(9)	32.5 (7)	C(28)-Nb(4)-C(29)	32.0 (7)	C(48)-Nb(6)-C(49)	33.0 (7)
C(9)-Nb(2)-C(10)	35.4 (6)	C(29)-Nb(4)-C(30)	34.9 (6)	C(49)-Nb(6)-C(50)	33.9 (7)
C(10)-Nb(2)-C(6)	36.3 (6)	C(30)-Nb(4)-C(26)	36.0 (6)	C(50)-Nb(6)-C(46)	36.3 (7)
		C-Nb-C(C_5H_5)			
C(11)-Nb(1)-C(12)	34.9 (7)	C(31)-Nb(3)-C(32)	34.6 (7)	C(51)-Nb(5)-C(52)	33.8 (7)
C(12)-Nb(1)-C(13)	33.4 (7)	C(32)-Nb(3)-C(33)	34.4 (7)	C(52)-Nb(5)-C(53)	32.3 (7)
C(13)-Nb(1)-C(14)	34.3 (7)	C(33)-Nb(3)-C(34)	34.0 (7)	C(53)-Nb(5)-C(54)	34.3 (6)
C(14)-Nb(1)-C(15)	33.7 (7)	C(34)-Nb(3)-C(35)	33.0 (7)	C(54)-Nb(5)-C(55)	33.8 (6)
C(15)-Nb(1)-C(11)	34.2 (7)	C(35)-Nb(3)-C(31)	34.6 (8)	C(55)-Nb(5)-C(51)	33.7 (7)
C(16)-Nb(2)-C(17)	35.3 (6)	C(36)-Nb(4)-C(37)	33.3 (7)	C(56)-Nb(6)-C(57)	33.1 (7)
C(17)-Nb(2)-C(18)	33.2 (6)	C(37)-Nb(4)-C(38)	33.9 (7)	C(57)-Nb(6)-C(58)	34.1 (7)
C(18)-Nb(2)-C(19)	34.0 (7)	C(38)-Nb(4)-C(39)	35.8 (8)	C(58)-Nb(6)-C(59)	33.7 (8)
C(19)-Nb(2)-C(20)	35.5 (7)	C(39)-Nb(4)-C(40)	35.0 (7)	C(59)-Nb(6)-C(60)	34.1 (7)
C(20)-Nb(2)-C(16)	33.5 (6)	C(40)-Nb(4)-C(36)	33.6 (7)	C(60)-Nb(6)-C(56)	33.5 (7)
		C-C-C(C_5H_4)			
C(5)-C(1)-C(2)	101.8 (18)	C(25)-C(21)-C(22)	101.3 (17)	C(45)-C(41)-C(42)	102.5 (17)
C(1)-C(2)-C(3)	114.3 (21)	C(21)-C(22)-C(23)	108.0 (17)	C(41)-C(42)-C(43)	111.3 (19)
C(2)-C(3)-C(4)	108.5 (21)	C(22)-C(23)-C(24)	110.6 (18)	C(42)-C(43)-C(44)	109.1 (19)
C(3)-C(4)-C(5)	107.8 (19)	C(23)-C(24)-C(25)	106.0 (19)	C(43)-C(44)-C(45)	106.2 (18)
C(4)-C(5)-C(1)	107.5 (18)	C(24)-C(25)-C(21)	114.0 (19)	C(44)-C(45)-C(41)	110.7 (18)
C(10)-C(6)-C(7)	104.4 (17)	C(30)-C(26)-C(27)	104.7 (18)	C(50)-C(46)-C(47)	99.0 (18)
C(6)-C(7)-C(8)	110.9 (17)	C(26)-C(27)-C(28)	110.2 (18)	C(46)-C(47)-C(48)	115.1 (20)
C(7)-C(8)-C(9)	110.2 (18)	C(27)-C(28)-C(29)	105.8 (19)	C(47)-C(48)-C(49)	104.0 (20)
C(8)-C(9)-C(10)	105.7 (19)	C(28)-C(29)-C(30)	112.3 (18)	C(48)-C(49)-C(50)	110.8 (21)
C(9)-C(10)-C(6)	108.8 (17)	C(29)-C(30)-C(26)	106.9 (18)	C(49)-C(50)-C(46)	111.0 (18)
		C-C-C(C_5H_5)			
C(15)-C(11)-C(12)	110.7 (17)	C(35)-C(31)-C(32)	106.8 (23)	C(55)-C(51)-C(52)	107.0 (22)
C(11)-C(12)-C(13)	104.8 (20)	C(31)-C(32)-C(33)	106.6 (21)	C(51)-C(52)-C(53)	111.6 (23)
C(12)-C(13)-C(14)	109.9 (22)	C(32)-C(33)-C(34)	107.4 (20)	C(52)-C(53)-C(54)	105.1 (19)
C(13)-C(14)-C(15)	109.3 (23)	C(33)-C(34)-C(35)	110.0 (21)	C(53)-C(54)-C(55)	110.2 (17)
C(14)-C(15)-C(11)	105.1 (20)	C(34)-C(35)-C(31)	109.1 (22)	C(54)-C(55)-C(51)	106.1 (19)
C(20)-C(16)-C(17)	109.2 (19)	C(40)-C(36)-C(37)	109.0 (22)	C(60)-C(56)-C(57)	112.8 (22)
C(16)-C(17)-C(18)	104.4 (19)	C(36)-C(37)-C(38)	109.7 (22)	C(56)-C(57)-C(58)	107.3 (23)
C(17)-C(18)-C(19)	112.8 (21)	C(37)-C(38)-C(39)	107.2 (21)	C(57)-C(58)-C(59)	104.4 (22)
C(18)-C(19)-C(20)	105.3 (20)	C(38)-C(39)-C(40)	105.6 (19)	C(58)-C(59)-C(60)	113.9 (22)
C(19)-C(20)-C(16)	108.3 (19)	C(39)-C(40)-C(36)	108.5 (22)	C(59)-C(60)-C(56)	101.6 (19)

Table VI. Distances and Angles for Average Monomer Structure $[(C_5H_5)(C_5H_4)NbH]$

	Distances, Å		
Nb(1)-Nb(2)	3.105 (6)	C-C(C_5H_5)	1.403 (5)
Nb(1)-C(1)	2.297 (3)	C-C(C_5H_4)	1.418 (7)
Nb(1)-C(2) or C(5)	2.332 (6)	C(1)-C(2) C(1)-C(5) } C_5H_4	1.443 (10)
Nb(1)-C(3) or C(4)	2.439 (8)		
Nb(1)-C(6)	2.232 (7)	C(2)-C(3) C(4)-C(5) } C_5H_4	1.418 (9)
Nb(1)-C(C_5H_5)	2.398 (4)		
Nb(1)-H	1.70 (3)	C(3)-C(4) C_5H_4	1.368 (10)
	Angles, deg		
Nb(2)-Nb(1)-C(1)	45.8 (2)	C-C-C(C_5H_4)	108.0 (7)
Nb(2)-Nb(1)-C(6)	47.6 (1)	C-C-C(C_5H_5)	108.0 (5)
Nb(1)-C(1)-Nb(2)	86.6 (3)		

[a] The distances and angles were averaged over the six monomeric units according to chemical equivalence and the errors estimated according to $[\Sigma^n(d_i - \overline{d})^2/n(n-1)]^{1/2}$ where d_i and $\overline{d}$ are the functions and mean function, respectively.

downfield from the other three. The structure, however, does not reveal one unique carbon atom. However, the structure does illustrate an unusual geometry for the hydrogens bound to C(2) and C(7). The bridging geometry forces a close contact between these hydrogens. The mean H-H distance for these hydrogens in their calculated positions is 1.90 Å. Also each hydrogen is positioned near the plane of the adjacent ring. These hydrogens are shown in Figure 2. The combined steric and ring current effects may cause this hydrogen to be shifted downfield from the other three in the nmr.

All the intermolecular contacts were calculated. The shortest observed contacts are 3.32 Å for C-C, 2.46 Å for C-H, and 2.29 Å for H-H with the hydrogens in calculated positions. The molecules are separated by normal van der Waals contacts.

Table VII. Least-Squares Planes for $[(C_5H_5)(C_5H_4)NbH]_2$

Plane no.	Equation and atoms[a]
1	$-0.2517X + 0.8382Y + 0.4838Z - 2.430 = 0$ C_5H_4: C1 (−0.018), C2 (0.007), C3 (0.009), C4 (−0.021), C5 (0.023), Nb1 (−2.027)
2	$-0.2434X + 0.1519Y + 0.9580Z + 0.080 = 0$ C_5H_4: C6 (−0.016), C7 (0.014), C8 (−0.006), C9 (−0.005), C10 (0.013), Nb2 (2.026)
3	$-0.4254X + 0.8860Y - 0.1845Z + 3.718 = 0$ C_5H_5: C11 (0.021), C12 (−0.028), C13 (0.025), C14 (−0.012), C15 (−0.006), Nb1 (2.074)
4	$-0.4782X - 0.4354Y + 0.7627Z - 3.085 = 0$ C_5H_5: C16 (0.005), C17 (−0.005), C18 (0.004), C19 (−0.001), C20 (−0.003), Nb2 (−2.082)
5	$0.5791X - 0.5784Y - 0.5745Z + 2.353 = 0$ C_5H_4: C21 (−0.013), C22 (0.003), C23 (0.009), C24 (−0.018), C25 (0.020), Nb3 (−2.045)
6	$0.1393X + 0.9062Y + 0.3993Z - 11.615 = 0$ C_5H_4: C26 (−0.002), C27 (0.011), C28 (−0.018), C29 (0.017), C30 (−0.009), Nb4 (−2.025)
7	$0.9705X - 0.1869Y - 0.1525Z - 1.093 = 0$ C_5H_5: C31 (0.003), C32 (−0.010), C33 (0.013), C34 (−0.012), C35 (0.006), Nb3 (2.080)
8	$0.4119X + 0.8826Y - 0.2267Z - 5.095 = 0$ C_5H_5: C36 (−0.015), C37 (0.016), C38 (−0.011), C39 (0.002), C40 (0.007), Nb4 (2.073)
9	$-0.3685X - 0.1495Y + 0.9175Z - 2.211 = 0$ C_5H_4: C41 (0.002), C42 (0.010), C43 (−0.018), C44 (0.019), C45 (−0.013), Nb5 (−2.032)
10	$0.4767X - 0.1962Y + 0.8569Z - 2.163 = 0$ C_5H_4: C46 (0.023), C47 (−0.020), C48 (0.009), C49 (0.007), C50 (−0.019), Nb6 (2.039)
11	$0.7644X - 0.2692Y - 0.5858Z + 0.846 = 0$ C_5H_5: C51 (−0.004), C52 (0.001), C53 (0.002), C54 (−0.004), C55 (0.005), Nb5 (−2.085)
12	$0.8542X + 0.1995Y + 0.4801Z - 12.896 = 0$ C_5H_5: C56 (0.002), C57 (0.006), C58 (−0.012), C59 (0.014), C60 (−0.010), Nb6 (−2.091)

	Dihedral Angles, deg			
	Molecule 1	Molecule 2	Molecule 3	Av
Nb(1)Nb(2)C(1) Nb(1)Nb(2)C(6)	53.3	49.0	53.4	51.9 (15)
C_5H_4(plane 1) C_5H_4(plane 2)	130.1	132.3	129.8	130.7 (8)
C_5H_4(plane 1) C_5H_5(plane 3)	139.5	139.3	141.2	140.4 (4)
C_5H_4(plane 2) C_5H_5(plane 4)	141.3	140.1	141.2	
Nb(1)–C(6) vector C_5H_4(plane 2)	58.6	57.3	57.8	58.4 (3)
Nb(2)–C(1) vector C_5H_4(plane 1)	59.0	58.8	59.0	

[a] The Nb atoms were not included in the planes; otherwise the atoms in the plane and their deviations from the planes are given below each plane.

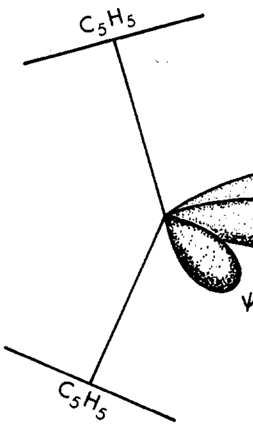

Figure 3. Idealized structure of bis(cyclopentadienyl)–transition metal complexes.

Table VIII. Selected Structures with Bis(π-cyclopentadienyl) Ligands

Compd	Angle C_5H_5–M–C_5H_5, deg
$(C_5H_5)_2MoH_2$[a]	34
$(C_5H_5)Mo(C_5H_4)Mn(CO)_4$[b]	35
$[(C_5H_5)(C_5H_4)NbH]_2$	39.6
$(C_5H_5)_3MnNO$[c]	43.3
$[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$[d]	44
$(C_5H_5)_2Ti(C_6H_5)_2$[e]	44
$(C_5H_5)_2W(SPh)_2Mo(CO)_4$[f]	45.5
$(C_5H_5)_2Ti\overbrace{C_6H_4COO}$[g]	46
$(C_5H_5)_2TiCl_2$[h]	46
$(C_5H_5)_2TiS_5$[i]	46.3
$[(CH_2)_3(C_5H_4)_2]TiCl_2$[j]	47.4
$(C_5H_5)_2MoS_2C_6H_3CH_3$[k]	47.5
$(C_5H_5)_2W(SPh)_2W(CO)_4$[f]	47.5
$(C_5H_5)_2TiC_3H_5$[l]	48.1
$(C_5H_5)_2W(SPh)_2Cr(CO)_4$[f]	48.5
$(C_5H_5)_2ZrCl(SiPh_3)$[m]	49.5
$(C_5H_5)_4Ti$[n]	50.1
$(C_5H_5)_2Ti(SMe)_2Mo(CO)_4$[f]	51.3
$(C_5H_5)_2ZrF_2$[o]	52.2
$(C_5H_5)_2ZrI_2$[o]	53.7
$(C_5H_5)_4Zr$,[p] av of 3	62.7

[a] M. Gerlock and R. Mason, *J. Chem. Soc.*, 296 (1965). [b] Reference 3. [c] J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, **91**, 2528 (1969). [d] Reference 4. [e] V. Kocman, J. C. Rucklidge, R. J. O'Brien, and W. Santo, *Chem. Commun.*, 1340 (1971). [f] T. S. Cameron, C. K. Prout, G. V. Rees, M. L. H. Green, K. K. Joshi, G. R. Davies, B. T. Kilbourn, P. S. Braterman, and V. A. Wilson, *ibid.*, 14 (1971). [g] I. S. Kolomnikov, T. S. Lobeeva, V. V. Gorbachevskaya, G. G. Aleksandrov, Yu. T. Struchkov, and M. E. Vol'Pin, *ibid.*, 972 (1971). [h] I. A. Ronova, N. V. Alekseev, N. I. Gapotchenko, and Yu. T. Struchkov, *J. Organometal. Chem.*, **25**, 149 (1970). [i] E. F. Epstein, I. Bernal, and H. Kopf, *ibid.*, **26**, 229 (1971). [j] B. R. Davis and I. Bernal, *ibid.*, **30**, 75 (1971). [k] J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 2013 (1969). [l] R. B. Helmholdt, F. Jellinek, H. A. Martin, and A. Vos, *Recl. Trav. Chim. Pays-Bas*, **86**, 1263 (1967). [m] K. W. Muir, *J. Chem. Soc.*, 2663 (1971). [n] J. L. Calderon, F. A. Cotton, B. G. De Boer, and J. Takats, *J. Amer. Chem. Soc.*, **93**, 3592 (1971). [o] M. A. Bush and G. A. Sim, *J. Chem. Soc.*, 2225 (1971). [p] Three π-bonded rings: V. I. Kulishov, E. M. Brainina, N. G. Bokiy, and Yu. T. Struchkov, *Chem. Commun.*, 475 (1970).

The novel bridging structure here allows both metal atoms to achieve an inert gas structure (18 electrons). If we view the formal oxidation state of niobium as IV (d^1 configuration) the Nb–Nb bond accounts for the observed diamagnetism.

The structure of $[(C_5H_5)(C_5H_4)NbH]_2$ can be viewed, in the valence bond language, in a way analogous to the description outlined by Ballhausen and Dahl[23] for protonated sandwich compounds. This approach views structures of bis(cyclopentadienyl)–transition metal complexes as having canted rings with three hybrid orbitals in the horizontal mirror plane as shown in Figure 3. Perhaps a better description would have ψ_2 displaced from the $\psi_1\psi_3$ plane,[24,25] but no differentiation is intended here with respect to the planarity or lack of planarity of these orbitals. Here Nb(1) has H in the ψ_1 position, C(6) in the ψ_2 position, and Nb(2) in the ψ_3 position; ψ_2 and ψ_3 are in the positions expected for the metal orbitals used in the "bent" bonds. Empirically the structure in Figure 3 is consistent with many transition metal complexes with two cyclopentadienyl rings; ψ_2 is used

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(24) J. C. Green, M. L. H. Green, and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 421 (1972).

(25) N. W. Alcock, *J. Chem. Soc. A*, 2001 (1967).

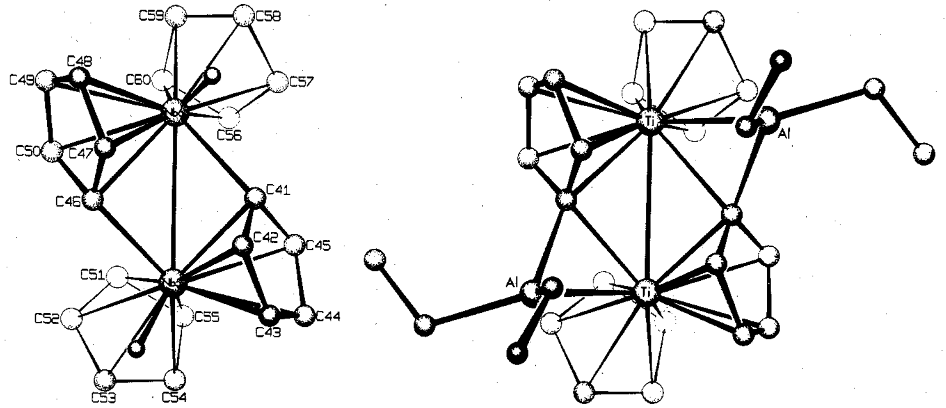

Figure 4. A comparison of the molecular structure of $[(C_5H_5)(C_5H_4)NbH]_2$ and $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$. The coordinates for the latter structure were taken from ref 4.

for one other ligand, ψ_2 and ψ_3 are used for two other ligands, and ψ_1, ψ_2, and ψ_3 are used for three other ligands. Other observed structures which can be generally rationalized in terms of the structure in Figure 3 are listed in Table VIII. Table VIII also lists the dihedral angles found between the cyclopentadienyl rings. The spread of nearly a factor of 2 in the dihedral angles illustrates the flexibility in this type of structure (Figure 3). Presumably other complexes, with as yet unknown structures, such as $(C_5H_5)_2NbH_3$, $(C_5H_5)_2Nb(H)PEt_3$, and $(C_5H_5)_2Nb(H)C_2H_4$[5] are also based on this type of structure.

The bridging geometry in $(C_5H_5)(CO)Mo(C_5H_4)Mn(CO)_4$ is similar to that found here for $[(C_5H_5)(C_5H_4)NbH]_2$; the shorter Mo-Mn distance (2.961 Å) results perhaps from the less rigid constraints of a single bridging C_5H_4 ligand. A comparison with the $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$ structure[4] is particularly interesting. The latter structure was reported to contain bridging C_5H_5 ligands in addition to terminal C_5H_5 ligands. A comparison with $[(C_5H_5)(C_5H_4)NbH]_2$ is shown in Figure 4. These accurately drawn coordinates show that the bridging geometries are the same for the two structures; the titanium structure must also contain bridging C_5H_4 ligands. Wailes and Weigold came to the same conclusion from chemical evidence.[26] The hydride hydrogen in the niobocene dimer is replaced by a bridging $(C_2H_5)_2Al$ in the $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$ structure.

We suggested the possibility of bridging C_5H_4 ligands for the titanocene dimer, $[(C_5H_5)(C_5H_4)TiH]_2$,[27] based on the similarities shown in Figure 4. Brintzinger and Bercaw[27] proposed bridging hydrogens for $[(C_5H_5)(C_5H_4)TiH]_2$ with terminal σ-bonded C_5H_4 ligands. Clearly a structure determination is needed on the titanocene dimer to establish the nature of the bridging structure.

Registry No. $[(C_5H_5)(C_5H_4)NbH]_2$, 11-105-934.

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Crystal Optics and Polarized Absorption Spectra for Tetraammineplatinum(II) Tetrachloroplatinate(II), Magnus' Green Salt

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The absorption spectra of small crystals of Magnus' green salt have been recorded at 300 and 15°K for light polarized in the directions of the *a* and *c* axes of the tetragonal crystals. In *a* polarization, a band at 25,000 cm^{-1} appears to be vibronically excited from the temperature dependence of its intensity. For *c* polarization, a band at *ca.* 16,500 cm^{-1} is also vibronically excited. There is no maximum in *c* polarization at 25,000 cm. Small crystals, about 10 μ thick and 10^{-2} mm^2 in cross section, had surfaces of sufficient optical quality that interference was observed in regions of low absorption for both polarizations. The indices of refraction could be determined by the shift in interference minima for crystals which were rotated in the beam. Values of the refractive indices are $n_a = 1.90 \pm 0.02$ and $n_c = 2.32 \pm 0.03$.

Introduction

Crystals of $[Pt(NH_3)_4][PtCl_4]$, Magnus' green salt (MGS), have a deep green color. Their color has attracted attention because many crystals and aqueous solutions of $PtCl_4^{2-}$ are red whereas solutions of $Pt(NH_3)_4^{2+}$ have negligible absorption in the visible region, and its simple salts are white. The green color can therefore be attributed to exceptional crystal effects. Atoji, Richardson, and Rundle[1] in a crystal structure determination by X-ray diffraction showed that MGS crystallizes in a tetragonal lattice with the space group *P4/mnc*, two molecular units per unit cell. In the crystals the ions stack alternately in chains along the *c* axis as shown

(1) M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Amer. Chem. Soc.*, 79, 3017 (1957).