Stereochemically Nonrigid Organometallic Molecules. XXVIII.[1] The Crystal and Molecular Structures of Tetra(cyclopentadienyl)titanium[2]

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Abstract: The crystal and molecular structures of tetra(cyclopentadienyl)titanium, $(C_5H_5)_4Ti$, have been determined from 1205 reflections, including 384 Friedel pairs, collected with a counter diffractometer. The compound crystallizes in the hexagonal space group $P6_122$ with six molecules, each lying on a twofold axis of rotation, in a unit cell of dimensions $a = b = 9.214 \pm 0.003$ Å, $c = 21.895 \pm 0.006$ Å ($\rho_{\text{calcd}} = 1.31$ g cm^{-3}). The structure, including hydrogen atoms, was solved from Patterson and electron density maps and refined by least-squares methods to a conventional unweighted R factor of 3.6%. The structure shows unambiguously that the molecule contains two *pentahapto-* and two *monohapto*cyclopentadienyl rings; the metal atom therefore has a 16-electron configuration. The distance from the h^5-C_3H_5 ring center to the titanium atom is 2.078 Å; individual Ti–C distances (Å) are: 2.381 (4), 2.359 (4), 2.373 (3), 2.391 (4), 2.400 (5). The other C_5H_5 ring is an exemplary *monohapto*cyclopentadienyl ring. The Ti–C distance is 2.332 (2) Å, and the C–C distances (Å), listed in order from the bound carbon atom around the ring, are: 1.446 (5), 1.360 (6), 1.420 (5), 1.355 (6), and 1.442 (3). The findings reported here lend considerable support to our claim that $(C_5H_5)_4Ti$ provides the first genuine example of the occurrence of rapid interchange of h^1-C_5H_5 and h^5-C_5H_5 rings as part of the fluxional behavior of the molecule.

Fluxional molecules are, by now, recognized to be of wide occurrence in the area of organometallic chemistry. Nevertheless, new molecules exhibiting new varieties of fluxional behavior are constantly being reported in the chemical literature. One such observation is the recent discovery of genuine *pentahapto-*, *monohapto*cyclopentadienyl ring exchange in tetra(cyclopentadienyl)titanium.[1,4,5]

To prove conclusively that such an exchange does indeed occur, it was considered essential to supplement studies[1,4] of the temperature dependence of the pmr spectra of $(C_5H_5)_4Ti$ with an X-ray crystallographic investigation which could demonstrate with great precision the relationship of the cyclopentadienyl rings to the titanium atom. To be consistent with our spectral findings and our explanations thereof, we had to show that the molecule contains two *pentahapto-* and two *monohapto*cyclopentadienyl groups.[9] The needed X-ray crystallographic investigation is reported in detail here.[11]

Experimental Section

Tetra(cyclopentadienyl)titanium was prepared as described elsewhere.[1] Suitable single crystals were grown by slow cooling of a toluene solution under nitrogen. The green-black crystals so obtained were truncated hexagonal bipyramids elongated along the c axis. The compound is air sensitive, and all subsequent X-ray work was performed on single crystals sealed in glass capillaries under nitrogen.

Single crystals, examined by Weissenberg ($hk0$, $hk1$, $hk2$) and precession ($h0l$) photographs, were found to be hexagonal. The systematic absences $00l$, $l \neq 6n$ and the $6/mmm$ Laué symmetry indicated one of the enantiomorphous space groups, $P6_122$ or $P6_522$. The following unit cell dimensions were obtained, at 23°, from 2θ values for $h00$ and $00l$ reflections which were carefully measured on a manually operated General Electric XRD-5 diffractometer using Cu Kα radiation ($\lambda(K\alpha_1)$ 1.5404 Å, $\lambda(K\alpha_2)$ 1.5443 Å): $a = b = 9.214 \pm 0.003$, $c = 31.895 \pm 0.006$ Å. The unit cell volume of 2345 Å^3 and $Z = 6$ gives $\rho_{\text{calcd}} = 1.31$ g cm^{-3}, a reasonable value for an organometallic compound. Unfortunately, the great reactivity of the compound prevented us from determining the density experimentally. With $Z = 6$, in either space group, the molecule must lie on a twofold axis of symmetry.

Intensity data were collected on the same diffractometer, equipped with a scintillation counter and a pulse-height discriminator which was set to accept 95% of the Cu Kα peak. To minimize multiple reflections,[12,13] the crystal was so aligned that the reflection (2,1,18) coincided with the φ axis of the instrument. The integrated intensities of 1205 reflections, including 384 Friedel pairs (*i.e.*, 821 Laué-independent reflections) within the sphere $\theta \leq 65°$ were measured using nickel-filtered copper radiation. The data were collected using a θ–2θ scan technique at a 2θ scan rate of 2°/min. The peak counts, P, were obtained from 40-sec 2θ scans, from

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[1] Part XXVII: J. L. Calderon, F. A. Cotton, and J. Takats, *J. Amer. Chem. Soc.*, **93**, 3587 (1971).

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[4] J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, **92**, 3801 (1970).

[5] The pmr spectra of the zirconium and hafnium analogs exhibit single sharp resonances even at −150°.[6] However, a recent structure determination of $(C_5H_5)_4Zr$[7] shows, contrary to the original claims,[8] that the molecule does not contain four h^5-C_5H_5 rings. Hence there is a strong possibility that very rapid interchange of different ring types does also occur in those molecules, the structural nature of which is still uncertain. (See, however, the Appendix to this paper.)

[6] F. A. Cotton and J. Takats, unpublished results.

[7] V. I. Kulishov, E. M. Brainina, N. G. Bokiy, and Yu. T. Struchkov, *Chem. Commun.*, 475 (1970).

[8] E. M. Brainina and G. G. Dvoryantserva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 442 (1967); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 427 (1967).

[9] Ring exchange has already been observed in $(C_5H_5)_3MoNO$.[10] However, it was found that two of the rings have geometries quite different from that of a normal h^5-C_5H_5 moiety, and it can be argued that such an arrangement of the rings predisposes them toward facile interchange with the h^1-C_5H_5 ring.

[10] J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, **91**, 2528 (1969).

[11] A preliminary account of this work has already appeared.[4]

[12] W. A. Zachariasen, *Acta Crystallogr.*, **18**, 705 (1965).

[13] When the crystal was aligned with c coincident with the φ axis, rapid fluctuations in intensity, from 0 to 1000 counts/sec, were observed at the position of the symmetry-forbidden 002 reflection as a function of ϕ (at $\chi = 90°$). Realignment to place (2, 1, 18) coincident with the ϕ axis was chosen to avoid, insofar as possible, such multiple-diffraction effects while retaining the great sensitivity to changes in crystal orientation which a reflection at $\chi = 90°$ affords.

$2\theta_{\text{calcd}} = -0.66°$ to $+0.67°$. Stationary background counts (B_1, B_2) of 20 sec each were taken at the limits of the scan. From these readings, the intensity, I, assuming a linear change in background, or its equivalent, is given by $I = P - (B_1 + B_2)$. Several strong reflections which exceeded the linear response range of the counter were remeasured with a lower X-ray tube current and were scaled to the other data by using medium-intensity reflections measured with both current settings. Periodic checks of four standard reflections showed a linear increase of intensity, to a maximum of about 7%, with time. Appropriate corrections to the intensities were applied. The standard deviation of an intensity, $\sigma(I)$, was defined as $\sigma(I) = [P + B_1 + B_2 + (pI)^2]^{1/2}$, where the "ignorance factor," p, was assigned a value of 0.025 for all except those reflections which were measured at a reduced X-ray tube current, where it was increased to 0.030 to account for the uncertainty in scaling. Any $I < 0.5[P + B_1 + B_2]^{1/2}$ was first set equal to $0.5[P + B_1 + B_2]^{1/2}$.

The 1205 reflections were corrected for Lorentz and polarization effects and a set of $|F_o|$ values, on a relative scale, was thus obtained. The standard deviation of an observed structure factor, $\sigma(|F_o|)$, was defined as $\sigma(|F_o|) = |F_o| - [(I - \sigma(I))/Lp]^{1/2}$ for $I > \sigma(I)$ and $\sigma(|F_o|) = [\sigma(I)/Lp]^{1/2}$ otherwise, where Lp is the Lorentz–polarization factor.

Appreciable variations (~15%) in the intensities of the (2,1,18) reflection were observed as a function of the crystal orientation. Consequently, absorption corrections ($\mu = 47.0$ cm^{-1}) based on the equations of the crystal faces were applied to the data. The transmission factors were in the range 0.436–0.281.

The crystal faces were identified as $(20\bar{2}3)$ and its symmetry-related family of 11 other planes, and the truncating faces were approximated by the 0001 and $000\bar{1}$ planes. The distances between opposite pairs of faces were: 0.29, 0.36, 0.30, 0.30, 0.31, and 0.26 mm; the distance between the (0001) and $(000\bar{1})$ faces was 0.47 mm.

Solution and Refinement of the Structure

The position of the titanium atom was found from a three-dimensional Patterson map. A subsequent three-dimensional electron density synthesis, phased by the titanium atom, revealed the location of all the nonhydrogen light atoms.

The structure was refined by conventional, full-matrix least-squares methods. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ is the observed and $|F_c|$ is the calculated structure amplitude, and the weighting factor, $w = [\sigma(|F_o|)]^{-2}$. Scattering factors were those of Cromer and Waber,[14] except for hydrogen atoms, for which those experimentally determined by Mason and Robertson[15] were used. Anomalous dispersion corrections to the scattering factors for titanium[16] and carbon[17] atoms were included in the calculation of the structure factors. Secondary extinction corrections were applied in the form[18] $F_c(\text{corr}) = F_c(1 - abI/A)$, where $b = q[2(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)^2]A^{-1}|\partial A/\partial\mu|$, A is the transmission factor, q is an approximate normalization constant,[18] and a was included as a parameter in the least-squares refinement.

Five cycles of isotopic least-squares refinement, including absorption and extinction corrections and using all the data, with the assumed space group $P6_122$, led to a discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.122$. The weighted residual, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, was 0.149. The ratios $|F_o(hkl)|/|F_o(khl)|$ were compared to the corresponding $|F_c|$ ratios and found to agree for the great majority of the reflections. The same comparison for the space group $P6_522$ revealed consistent disagreement. Hence the assumed space group, $P6_122$, was taken as the true one and refinement was continued in this space group. A difference Fourier map computed after two more cycles of refinement, in which the titanium atom and the carbon atoms of the h^1-C_5H_5 group were assigned anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and the carbon atoms of the h^5-C_5H_5 ring were refined isotopically, revealed the positions of the five hydrogen atoms of the *monohapto*cyclopentadienyl moiety. After two further cycles of refinement where all atoms other than hydrogen were assigned anisotropic temperature factors, an examination of another difference Fourier map permitted the location of the hydrogen atoms attached to the *pentahapto*-cyclopentadienyl ring. Three final cycles of refinement of positional and thermal parameters for all atoms resulted in convergence with $R_1 = 0.036$ and $R_2 = 0.040$.[19] A Hamilton R factor test[20] validated both the anisotropic model and the model including hydrogen atoms at the 99.5% confidence level.

The last cycle of refinement showed no parameter shift greater than one-fifth of its estimated standard deviation, except for a few hydrogen atoms where shifts of one-third of an estimated standard deviation were observed. The highest peak in the difference Fourier function computed at this point was 0.29 e/Å^3. The weighting scheme satisfies Cruickshank's criterion,[21] as $\Sigma w[|F_o| - |F_c|]^2$ was substantially the same in different ranges of both $|F_o|$ and $\sin\theta/\lambda$. The final standard deviation of an observation of unit weight was 1.61, indicating a slight underestimation of the standard deviations of the intensity data.

The following programs for the IBM 360 computer were used in this structure analysis and interpretation: (1) J. A. Ibers' PICK, 1966, for refining cell constants and generating angular settings for data collection; (2) A. Zalkin's Fourier analysis program FORDAP, modified by B. M. Foxman and L. N. Becka; (3) a modified version of C. T. Prewitt's full-matrix least-squares program SFLS5, 1966; (4) B. G. DeBoer's DRAB70, 1970, absorption corrections, secondary extinction parameters and data reduction; (5) J. S. Wood's MGEOM, 1964, molecular geometry with estimated standard deviations; (6) D. P. Shoemaker and R. C. Srivastava's DISTAN, 1963, crystallographic bond distance and dihedral angle program; (7) C. J. Johnson's ORTEP, 1965, Fortran thermal ellipsoid plot program for crystal structure illustrations; (8) R. C. Elder's PUBTAB, data presentation program.

Results

A table of the observed and final calculated structure amplitudes (electrons), multiplied by 10, for $(C_5H_5)_4Ti$ has been deposited with the ACS Publications Microfilm

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

(15) R. Mason and G. B. Robertson, *Advan. Struct. Res. Diff. Methods*, 2, 57 (1966).

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

(17) D. T. Cromer and D. Liberman, 8th International Congress of the International Union of Crystallography, Stony Brook, N. Y., Aug 1969.

(18) W. H. Zachariasen, *Acta Crystallogr.*, 16, 1139 (1963). Note that in eq 15 the normalizing A^* ($2\theta = 0$) is single valued only for the spherical-crystal case.

(19) The final value of R_2 as quoted was obtained by rejecting the reflection (419). We assume that some angle was misset when this reflection was measured, since its $|F_o|$ is much less than $|F_c|$ and no similar difficulty is encountered with the equivalent (149) reflection.

(20) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(21) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, Elmsford, N. Y., 1965, p 113.

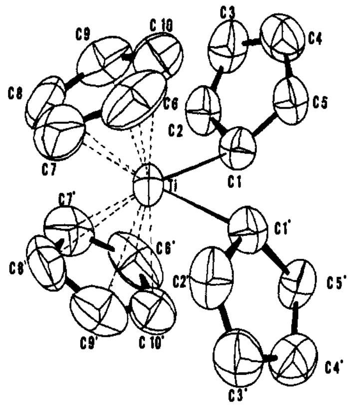

Figure 1. The $(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2Ti$ molecule, showing the structure and the atom numbering. A given number primed and unprimed designates a pair of atoms related by a crystallographic twofold axis. The atoms are represented by their thermal vibration ellipsoids.

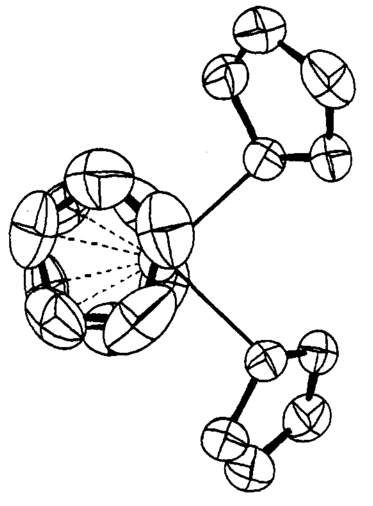

Figure 2. A view of the $(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2Ti$ molecule which shows the staggered configuration of the $h^5\text{-}C_5H_5$ rings.

Table I. Final Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	B, Å$^{2\,b}$
Ti	0.64549 (3)	0.29099 (6)[c]	0.25000 (0)[c]	3.74 (02)
C_1	0.0778 (3)	0.4621 (3)	0.0385 (1)	4.27 (09)
C_2	0.1581 (3)	0.4198 (4)	0.0056 (1)	5.53 (12)
C_3	0.0983 (4)	0.2517 (5)	0.0072 (1)	6.85 (15)
C_4	−0.0250 (4)	0.1800 (4)	0.0391 (1)	6.26 (14)
C_5	−0.0398 (3)	0.3045 (3)	0.0576 (1)	5.09 (10)
C_6	0.3251 (5)	0.8165 (4)	0.0240 (1)	7.60 (17)
C_7	0.4829 (5)	0.8377 (5)	0.0344 (1)	7.07 (16)
C_8	0.5238 (4)	0.9178 (4)	0.0725 (1)	7.01 (15)
C_9	0.3976 (6)	0.9413 (5)	0.0850 (1)	7.40 (17)
C_{10}	0.2772 (5)	0.8815 (5)	0.0564 (1)	7.16 (17)
H_1	0.052 (3)	0.551 (4)	0.034 (1)	5.7 (5)
H_2	0.240 (4)	0.498 (4)	−0.012 (1)	7.4 (7)
H_3	0.134 (4)	0.203 (4)	−0.012 (1)	8.8 (8)
H_4	−0.090 (4)	0.064 (4)	0.045 (1)	7.1 (7)
H_5	−0.127 (4)	0.290 (4)	0.078 (1)	8.2 (8)
H_6	0.280 (5)	0.778 (5)	0.003 (1)	9.5 (10)
H_7	0.541 (4)	0.803 (5)	0.019 (1)	8.5 (9)
H_8	0.623 (4)	0.939 (4)	0.088 (1)	8.1 (9)
H_9	0.387 (6)	0.986 (7)	0.105 (1)	10.8 (15)
H_{10}	0.163 (7)	0.875 (7)	0.059 (1)	13.6 (15)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digit listed. [b] The "equivalent" isotropic thermal parameters given for atoms other than hydrogen atoms were calculated by SFLS5 from the anisotropic temperature factors listed in Table II. [c] Symmetry constraints on the Ti parameters are $y = 2x$ and $z = 1/4$.

Table II. Anisotropic Temperature Factors[a] (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti	170 (1)	105 (1)	9.11 (6)	52 (1)[b]	−6 (0)	0 (0)[b]
C_1	148 (4)	202 (5)	8.9 (3)	79 (4)	−2 (1)	−4 (1)
C_2	170 (5)	281 (7)	10.2 (3)	84 (5)	2 (1)	−8 (1)
C_3	210 (6)	307 (8)	17.9 (5)	127 (6)	−1 (1)	−31 (2)
C_4	210 (6)	195 (6)	17.8 (4)	66 (4)	−6 (1)	−13 (1)
C_5	148 (4)	203 (5)	12.2 (3)	47 (3)	2 (1)	−8 (1)
C_6	365 (10)	188 (6)	11.4 (4)	18 (6)	−16 (2)	18 (1)
C_7	272 (8)	231 (7)	18.1 (5)	96 (6)	38 (2)	22 (2)
C_8	174 (5)	201 (6)	21.8 (6)	16 (4)	−5 (1)	12 (2)
C_9	357 (10)	196 (6)	16.3 (4)	93 (6)	12 (2)	5 (1)
C_{10}	244 (7)	226 (7)	22.0 (6)	100 (6)	16 (2)	30 (2)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digits listed. [b] Symmetry constraints on the Ti parameters are $\beta_{22} = 2\beta_{12}$ and $\beta_{23} = 0$.

Table III. Bond Distances[a]

Atoms	Distance, Å	Atoms	Distance, Å
Ti–C_1	2.332 (2)	C_1–C_2	1.446 (5)
Ti–C_6	2.381 (4)	C_2–C_3	1.360 (6)
Ti–C_7	2.359 (4)	C_3–C_4	1.420 (5)
Ti–C_8	2.373 (3)	C_4–C_5	1.355 (6)
Ti–C_9	2.391 (4)	C_5–C_1	1.442 (3)
Ti–C_{10}	2.400 (5)	C_6–C_7	1.407 (7)
		C_7–C_8	1.373 (6)
		C_8–C_9	1.346 (7)
		C_9–C_{10}	1.327 (6)
		C_{10}–C_6	1.373 (7)
C_1–H_1	0.97 (4)	C_6–H_6	0.77 (4)
C_2–H_2	0.93 (3)	C_7–H_7	0.89 (5)
C_3–H_3	0.92 (5)	C_8–H_8	0.98 (4)
C_4–H_4	0.95 (3)	C_9–H_9	0.79 (6)
C_5–H_5	0.99 (4)	C_{10}–H_{10}	1.03 (7)

[a] Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Depository Service.[22] The molecular structure and atom numbering system are shown in Figure 1. A projection of the molecule which reveals the staggered relation of the two $h^5\text{-}C_5H_5$ groups is shown in Figure 2.

Final atomic positions and thermal parameters are given in Table I, with the listed standard deviations being derived from the inverse matrix of the final least-squares refinement cycle. The hydrogen atoms are labeled according to the carbon atoms to which they are bonded (*i.e.*, H_i is bonded to C_i). Anisotropic thermal parameters are listed in Table II. Intramolecular distances and bond angles are given in Tables III and IV, while Table V gives the equations for the planes through the cyclopentadienyl rings and the distances of pertinent atoms from them.

Discussion

The most significant result of this investigation is the unequivocal demonstration that in the crystalline state[23] the $(C_5H_5)_4Ti$ molecule has a structure which con-

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(22) This table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(23) It should be noted that, to date, *every* fluxional organometallic molecule for which the requisite data are available has an instantaneous structure in solution which is consistent with the structure found for it in the crystalline state.

Table IV. Bond Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
Ti–C_1–C_2	106.4 (1)	Ti–C_1–C_5	114.1 (1)
C_1–Ti–C_1'	86.3	c.o.g.–Ti–c.o.g.[b]	129.9
C_2–C_1–C_5	105.2 (2)	C_6–C_7–C_8	105.7 (1)
C_1–C_2–C_3	108.0 (2)	C_7–C_8–C_9	108.8 (2)
C_2–C_3–C_4	109.3 (2)	C_8–C_9–C_{10}	109.8 (2)
C_3–C_4–C_5	108.2 (3)	C_9–C_{10}–C_6	108.4 (2)
C_4–C_5–C_1	109.1 (2)	C_{10}–C_6–C_7	107.3 (1)
C_5–C_1–H_1	122 (1)	C_{10}–C_6–H_6	129 (1)
C_2–C_1–H_1	120 (2)	C_7–C_6–H_6	124 (3)
C_1–C_2–H_2	124 (2)	C_6–C_7–H_7	125 (2)
C_3–C_2–H_2	128 (2)	C_8–C_7–H_7	129 (2)
C_2–C_3–H_3	120 (2)	C_7–C_8–H_8	123 (1)
C_4–C_3–H_3	131 (2)	C_9–C_8–H_8	127 (2)
C_3–C_4–H_4	126 (1)	C_8–C_9–H_9	131 (2)
C_5–C_4–H_4	126 (2)	C_{10}–C_9–H_9	119 (4)
C_4–C_5–H_5	126 (2)	C_9–C_{10}–H_{10}	125 (1)
C_1–C_5–H_5	124 (1)	C_6–C_{10}–H_{10}	126 (2)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digits listed. [b] c.o.g. denotes the center of gravity of the h^5-C_5H_5 group.

Table V. Best Weighted Least-Squares Planes[a]

Atoms	Plane	*L*	*M*	*N*	*D*
C_1–C_5	1	0.7086	−0.2638	0.6544	0.2009
C_6–C_{10}	2	−0.4383	−0.7733	0.4581	−5.4408

Distances of Atoms from Planes, Å			
Atoms	Plane 1	Atoms	Plane 2
C_1	0.014	C_6	−0.006
C_2	−0.018	C_7	0.006
C_3	0.012	C_8	−0.005
C_4	0.006	C_9	0.002
C_5	−0.013	C_{10}	0.002
Ti	1.968	Ti	2.078

[a] The equations of the planes are $LX + MY + NZ = D$, where L, M, and N are direction cosines referred to the orthogonal axis system a, b^*, c and $X = ax$, $Y = by$, and $Z = cz$.

sists of two *monohapto*- and two *pentahapto*cyclopentadienyl rings bound to the titanium atom. This is the type of structure considered necessary to account for the temperature-dependent pmr spectrum of the substance in solution.[1] The overall crystal structure consists of a closely packed array of these $(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2Ti$ molecules, each lying on a crystallographic twofold axis of rotation. The van der Waals contacts are all normal, and no major feature of the molecular structure appears attributable to intermolecular forces.

The rings are disposed about the titanium atom in a roughly tetrahedral way, but substantial distortions exist. Thus the C_1–Ti–C_1' angle is 86.3°, while the angle subtended at the titanium atom by the centroids of the h^5-C_5H_5 rings is 129.9°. These angles are not unlike the comparable ones found in similar molecules. For example it is reported[24] that in $(h^5\text{-}C_5H_5)_2TiS_5$ the S–Ti–S angle is 94.6° and the centroid-to-Ti-to-centroid angle is 133.6°, while in $[(h^5\text{-}C_5H_5)_2TiAl(C_2H_5)_2]_2$ the corresponding angles[25] are 91.8 and 133.6°.

The $(h^5\text{-}C_5H_5)$M group may be added to the small but lately increasing number of such moieties which are well characterized structurally. Although the C–C distances vary from 1.327 to 1.407 Å (individual esd's of 0.007 Å) and the C–C–C angles are in the range 105.7–109.8° (individual esd's of 0.2°), these variations are probably not real, but artifacts attributable to the liberational motion of the ring. The cyclopentadienyl ring itself is rigorously planar, no atom deviating from the mean plane by more than 0.006 Å. The symmetrical metal-to-ring bonding is most clearly evident in the titanium-to-carbon bond lengths which fall in the narrow range from 2.359 to 2.400 Å. A slight tilt of the h^5-C_5H_5 moiety with respect to the Ti–(C_5H_5 centroid) vector (~2°) accounts for the variations in the bond lengths. For a contrast to these small variations, we may refer to $(C_5H_5)_3MoNO$,[10] where the Mo–C distances to two of the rings vary from 2.32 to 2.68 Å, a range of 0.40 Å. In this case a form of bonding basically different from that in a true $(h^5\text{-}C_5H_5)$M group is believed to exist.

The titanium atom lies 2.078 Å from the mean plane of the *pentahapto*cyclopentadienyl carbon atoms. This and the Ti–C distances are very similar to those found in other titanium compounds containing h^5-C_5H_5 groups, such as $(C_5H_5)_2TiS_5$,[24] $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$,[25] and $(h^5\text{-}C_5H_5)_2TiCl_2$.[26] The two symmetry-related h^5-C_5H_5 rings have a nearly staggered relationship (much like a pair of bevel gears) as shown in Figure 2, presumably because of nonbonded interactions between them.

It is noteworthy that this is one of the few cases in which the occurrence of an essentially symmetrical M–C_5H_5 interaction (C_{5v} symmetry) has actually been demonstrated crystallographically. There is, of course, no doubt that many other examples exist even though rotational disorder or other complications may interfere with the unequivocal crystallographic demonstration of it. To put it another way, there are many cases where a true *pentahapto*cyclopentadienylmetal grouping may reasonably be presumed to exist even though crystallographic results fall short of giving a neat and accurate representation of this. Ferrocene itself is an example of this situation.[27] On the other hand, we consider it important to call attention to the fact that there can be cases where crystallographically obtained dimensions which are considerably at variance with those ideally expected for an $(h^5\text{-}C_5H_5)$M grouping should *not* be ignored and the conclusion drawn that a regular $(h^5\text{-}C_5H_5)$M grouping exists despite the lack of satisfactory evidence. This is especially true because it is now proven that a genuine intermediate bonding situation such as that found in $(C_5H_5)_3MoNO$ can exist. With regard to this point and because of its kinship to $(C_5H_5)_4Ti$, we discuss in the Appendix the recently reported[7] X-ray structural study of $(C_5H_5)_4Zr$.

The other two cyclopentadienyl groups are well-defined monohapto types. The Ti–C_1 distance is 2.332 Å. The C–C bond lengths vary systematically around the ring in a manner consistent with the diene structure; *viz.* (starting at the carbon atom bound to Ti): 1.446, 1.360, 1.420, 1.355, and 1.442 Å. The C–C–C angle at the unique carbon atom is 105.2°, while the other four angles are very nearly equal with a mean value of 108.5°. The ring is planar; no carbon atom deviates from the mean plane by more than 0.018 Å. All these features are remarkably similar to corresponding ones for the h^1-C_5H_5 ring in $(C_5H_5)_3MoNO$, which is the only other

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(24) E. F. Epstein and I. Bernal, *Chem. Commun.*, 410 (1970), and private communications from Dr. Bernal.

(25) P. Corradini and A. Sirigu, *Inorg. Chem.*, **6**, 601 (1967).

(26) N. V. Alekseev and I. A. Ronova, *Zh. Strukt. Khim.*, **7**, 103 (1966); *J. Struct. Chem. (USSR)*, **7**, 91 (1966).

(27) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).

accurately characterized h^1-C_5H_5 ring known to us, though several others have been observed with lower accuracy.

With respect to the planarity of the h^1-C_5H_5 ring as we have observed it now in two cases, in both of which the accuracy of the structures attains, approximately, the normal or practical limit, we would stress that *there is no significant dihedral bend across the C_2–C_5 line.* The dihedral angle between the $C_2C_3C_4C_5$ and $C_5C_1C_2$ planes is 2.2 ± 0.9°. In the h^1-C_5H_5 ring of $(C_5H_5)_3$-MoNO the same angle is <1°. Thus, these accurate results for h^1-C_5H_5 rings imply that such a bend is not a significant or characteristic feature of h^1-C_5H_5 rings bound to metal atoms.

Recently, in at least two papers[28,29] Russian workers claim to have discovered a new geometry for the h^1-C_5H_5 group, the so-called "envelope" conformation. The angle of fold they report in $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$-$Sn(h^1\text{-}C_5H_5)_2$[28] is 27°, while in $(CH_3)_3Si(h^1\text{-}C_5H_5)$[29] the reported value is 22°. Both of these figures should be very significantly different from 0° even for structures of average quality. Although we do not doubt the result of the structural analysis, we refute their contention[28] that: "*As usual* (italics ours) for substituted cyclopentadienyl rings, the carbon atoms bearing the substituents lie out of the plane of the remaining four carbon atoms of their own ring, and consequently the rings take on the form of an envelope." Indeed, quite elementary considerations of the hybridization of the carbon atoms would lead one to expect an essentially planar cyclopentadienyl ring for an h^1-C_5H_5 moiety. We might also point out that the series of "cyclopentadienyl" complexes[30–33] selected by Biryukov and Struchkov to buttress their contention is inappropriate. Their tabulation refers to special cases in which the bent C_5 ring, in addition to being α substituted, is bound to a transition metal, in a direction approximately normal to the ring, by a combination of metal–olefin interactions and metal–carbon σ bonds. As a result of this, the hybridization of two of the ring carbon atoms changes from sp^2 toward sp^3 with a concommitant, and entirely expected, folding of the cyclopentadienyl ring. But this is wholly irrelevant to the nature of an otherwise free h^1-C_5H_5 ring.

Finally we would like to discuss the location and the refinement of the hydrogen atoms. It is not surprising to find that the range of C–H bond lengths and the values of the isotropic temperature factors reflect the nature of the cyclopentadienyl ring group to which the hydrogen atoms are bound. The hydrogen atoms of the h^5-C_5H_5 show considerable variations in the C–H bond distances, ranging from 0.77 to 1.07 Å, and the temperature factors are relatively large (see Table I). Nevertheless, the refinement was convergent, which is very satisfying considering the libration of the pentahapto ring. For the h^1-C_5H_5 ring, the range of C–H bond lengths is quite narrow, 0.92–0.99 Å, with the temperature factors about 30% greater than those for the carbon atoms to which they are attached. The mean C–H distance of 0.95 ± 0.04 Å is in very good agreement with accurately determined values in $(h^5\text{-}C_5H_5)$-$CuP(C_6H_5)_3$.[34]

Acknowledgment. We wish to thank Dr. Marie D. LaPrade for some useful discussions.

Appendix

Kulishov, *et al.*,[7] have recently described an X-ray crystallographic study of $(C_5H_5)_4Zr$ and concluded that it contains one h^1-C_5H_5 and three h^5-C_5H_5 rings.[34a] We suggest that such a structure is not justified by their data nor is it plausible on the basis of general bonding considerations. The crystallographic results appear to show definitely that there is one h^1-C_5H_5 ring present, but the nature of the remaining three is left uncertain by the crystallographic results *per se*. Thus, for these three rings it is reported that the Zr–C distances vary from 2.49 to 2.73 Å, with individual values having esd's of 0.02 Å. Such a spread of distances, when all are supposed to be equal, could only indicate (a) that the crystallographic work is very crude (in which case a claim for esd's of 0.02 Å would be unjustified) *or* (b) that the rings concerned are not in fact true h^5-C_5H_5 rings and that the spread of Zr–C distances is real.

We suggest that while the crystal structure as reported may indeed leave something to be desired in comparison with contemporary standards of accuracy (perhaps owing entirely to problems with poor crystal quality over which the authors had no control), the main point is probably that *there are not three h^5-C_5H_5 rings present.* If there were, the effective atomic number of the zirconium atom would be 4 + 1 + 3(5) = 20. This is not credible to us. We specifically propose that $(C_5H_5)_4Zr$ contains one h^1-C_5H_5 ring, one h^5-C_5H_5 ring, and two of the severely tilted rings found in $(C_5H_5)_3MoNO$. The latter two can, as already proposed,[35] be considered to involve two Mo–C bonds of roughly order 1.0, one somewhat weaker (say, order 0.8), and two distinctly weaker, of order ∼0.6. Adding these fractional orders, one obtains 4.0, so that one might say, crudely, and in a very formal sense, that such a severely tilted ring is a four-electron donor. Thus, in $(C_5H_5)_3MoNO$, treating the NO group as a three-electron donor, the h^1-C_5H_5 group as a one-electron donor, and the severely tilted rings as four-electron donors, we get a total electron count at the Mo atom of 6 + 3 + 1 + 2(4) = 18. In an exactly analogous way, for $(C_5H_5)_4Zr$ we may write 4 + 5 + 1 + 2(4) = 18. We postulate that the three C_5H_5 rings described by Kulishov, *et al.*, as all pentahapto will be found on closer inspection and more careful interpretation of suitably accurate structural data to include one true h^5-C_5H_5 ring and two of the severely tilted type of ring already found and fully described in $(C_5H_5)_3MoNO$.

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(28) B. P. Biryukov and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 95 (1969); *J. Struct. Chem.* (*USSR*), 10, 86 (1969).

(29) N. N. Veniaminov, Yu. A. Ustynizuk, N. V. Aleksev, I. A. Ronova, and Yu. T. Struchkov, *J. Organometal. Chem.*, 22, 551 (1970).

(30) $[(F_3C)_4C_5O]Co(C_5H_5)$: M. Gerloch and R. Mason, *Proc. Roy. Soc.*, *Ser. A*, **279**, 170 (1964).

(31) $(C_6H_5\text{–}C_5H_5)Co(C_5H_5)$: M. R. Churchill and R. Mason, *ibid.*, *A*, **279**, 191 (1964).

(32) $(h^5\text{-}C_5H_5CoC_5H_5\text{–})_2C_6H_4$: O. V. Starovskii and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **6**, 248 (1965); *J. Struct. Chem.* (*USSR*), 6, 228 (1965).

(33) $[(F_3C)_4C_5O]Fe(CO)_3$: N. A. Bailey and R. Mason, *Acta Crystallogr.*, 21, 652 (1966).

(34) F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, **92**, 2353 (1970).

(34a) Note Added in Proof. From the brief account given in ref 7, it was merely our conjecture that the structure determination was very unreliable except as to gross features. A more complete report which has now appeared [V. I. Kulishov, N. G. Bokii, and Y. T. Struchkov, *J. Struct. Chem.* (*USSR*), **11**, 646 (1970)] removes all doubt.

(35) F. A. Cotton, *Discuss. Faraday Soc.*, No. **47**, 79 (1969).

It may be noted further that the presence in one molecule of an h^5-C_5H_5 ring, an h^1-C_5H_5 ring, and two with an intermediate relationship to the metal might reasonably be expected to lead to ready interchange of ring types, since the intermediate ones can, as demonstrated in $(C_5H_5)_3MoNO$, readily interchange with the h^1-C_5H_5 type of ring and it seems obvious that they could, perhaps even more easily, exchange roles with the h^5-C_5H_5 ring. Thus, our observation[6] that site exchange of all 20 protons in $(C_5H_5)_4Zr$ (and the hafnium analog) persists down to low temperatures in solution is well accounted for by the structure we are proposing.

That $(C_5H_5)_4Zr$ adopts a structure in which an effective 18-electron population is achieved at the metal atom, whereas $(C_5H_5)_4Ti$ has only a 16-electron population, seems naturally attributable to the fact that the structure giving the higher population is sterically more demanding and only the larger metal atom can meet the requirements.

Crystal and Molecular Structure of Bis(dithiotropolonato)nickel(II)

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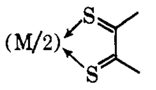
Abstract: The crystal and molecular structure of bis(dithiotropolonato)nickel(II), $Ni(S_2C_7H_5)_2$, has been determined from three-dimensional single-crystal X-ray diffraction data collected by the θ-2θ counter technique. The neutral complex crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5, no. 14) in a cell of dimensions $a = 7.845$ (10), $b = 13.638$ (20), $c = 6.913$ (10) Å, $\beta = 97°\,13\,(2)'$, and $V = 733.9$ Å^3. There are two molecules of the complex per unit cell ($\rho_{\text{exptl}} = 1.62 \pm 0.03$ g/cm^3 and $\rho_{\text{calcd}} = 1.65$ g/cm^3 for $Z = 2$). All atoms including hydrogens have been located, and their positional and thermal parameters have been refined by least-squares methods to a conventional R factor of 0.024 for 976 independent reflections. The complex is required to possess a center of symmetry and the coordination geometry is necessarily planar. The average Ni–S distance is 2.147 (3) Å with a S–Ni–S intrachelate ring bond angle of 90.11 (5)°. It is found that the C–C bond which is common to both the chelate ring and the tropolone ring is significantly longer (1.448 (4) Å) than the other carbon–carbon ring distances (1.378–1.401 (4) Å). This result is consistent with the previously reported chemical properties of $Ni(S_2C_7H_5)_2$ and underscores the lack of dithiolene character in this complex.

During the last several years, metal chelates containing the class of ligands known generically as the 1,2-dithiolenes or 1,2-dithienes have been extensively studied, and recently, several reviews of these systems have appeared.[1,2] Complexes of the 1,2-dithiolenes have received this considerable attention principally because of the relatively facile and reversible electron-transfer reactions which they undergo, and because of the extended π systems and electron delocalization which are characteristic of their ground states.

Particular attention in this area has been directed to the monomeric bis complexes which are found to possess the square-planar geometry for a wide variety of metal ions and d-electron configurations.[3,4] The interesting and unusual properties of metal 1,2-dithiolenes have generally been attributed to the formation of unsaturated five-membered chelate rings and the effective overlap of the metal d functions with the π molecular orbitals of the ligand. A valence-bond description of the electronic structures of the dithiolene complexes requires resonance structures of types I and II[1,2] which may be weighted according to the overall charge on the complex, the relative ligand and metal reduction potentials, the degree of delocalization, and various other factors.



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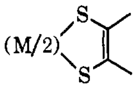
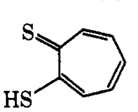
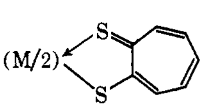


II

Recently, Forbes and Holm synthesized and characterized dithiotropolone (III) and a number of bis complexes of the dithiotropolonate anion.[5] Their study of complexes of type IV was based in simplest terms on the notion that the dithione and dithiolate resonance structures I and II, which are of fundamental importance for the dithiolene complexes, play only a minor role in describing the electronic structures of the correspond-



III



IV

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(1) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

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