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X-Ray Structure Analysis of $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$

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The structure of $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ has been determined from a three-dimensional X-ray analysis. The molecular crystals contain four dimeric molecules in a unit cell of symmetry Pbcn and dimensions $a = 9.50 \pm 0.02$ A, $b = 14.60 \pm 0.03$ A, and $c = 19.40 \pm 0.03$ A. Each dimeric molecule consists of two units of $(C_5H_5)_2TiAl(C_2H_5)_2$ linked through a Ti–Ti bond which intersects a twofold symmetry axis. Each Ti atom is also coordinated to two π-cyclopentadienyl rings and to an Al atom. Furthermore, both Ti and Al atoms of one unit $(C_5H_5)_2TiAl(C_2H_5)_2$ are at bonding distance from one carbon atom of one of the two π-cyclopentadienyl rings of the other unit related by a twofold symmetry axis. The structure of the molecule and the nature of bonding are discussed.

Introduction

The study of the structure of complexes containing Al and Ti atoms is of great interest in order to elucidate the mechanisms of stereospecific polymerization.

In this work we have examined by three-dimensional X-ray methods the structure of $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ prepared first by Natta, *et al.*[1]

Experimental Data

Lattice parameters and space group were determined from Weissenberg photographs taken with Cu Kα radiation: $a = 9.50 \pm 0.02$ A, $b = 14.60 \pm 0.03$ A, and $c = 19.40 \pm 0.03$ A. The observed systematic absences uniquely defined the centrosymmetric space group Pbcn (D_{2h}^{14}), which was subsequently verified by the structural analysis.

Three-dimensional intensity data were recorded from multifilm-equiinclination Weissenberg photographs. In order to reduce the absorption effects Mo Kα radiation was used (μ/ρ(Ti) = 24.2 for Mo Kα, 208 for Cu Kα).[2]

The intensities of 744 nonzero reflections (0*kl*–5*kl*, *h*0*l*–*h*6*l*) were measured by visual comparison with a standard scale. Some low-angle reflections (starred in Table I) that were not accessible with Mo Kα radiation were obtained with Cu Kα radiation. A correction for absorption was made for these reflections assuming cylindrical shape for a prismatic crystal of 0.3 × 0.2 mm cross section.

After the usual corrections were applied the reflections were put into a common scale following the method of Rollet and Sparks.[3]

Determination and Refinement of the Structure

Preliminary atomic coordinates were obtained from a previous Patterson analysis and successive two-dimensional Fourier syntheses.[4]

A structure factor calculation made with these original coordinates yielded an *R* factor of 0.21 for the 744 observed reflections.

A three-dimensional Fourier synthesis was then computed from which new atomic coordinates were obtained which decreased *R* to 0.19. Refinement of the structure was carried out by means of differential synthesis calculations. After four cycles of refinement, the *R* factor was 0.145. Although the shifts in the coordinates of some carbon atoms in the last cycle were still of the same order of magnitude as the corresponding standard deviations, their changes did not lead to a further significant lowering of the *R* factor. Hence, refinement was terminated at this point.

Anisotropic treatment of the temperature factors was made for the Ti and Al atoms only, since such a treatment proved to be statistically insignificant for the carbon atoms. Hydrogen atoms were included in the final structure factor calculation. Their positions were calculated from stereochemical considerations, and no attempt was made to locate them by a difference Fourier synthesis calculation. The final *R* factor was 0.140. Observed and calculated structure factors at the final stage are reported in Table I. For all calculations an IBM 1620 computer was used. Programs were kindly supplied by Giglio and Damiani.[5]

Final atomic coordinates and the relative standard deviations are given in Table II.[6] In the same table the isotropic temperature factors of the carbon atoms and the anisotropic ones of Ti and Al atoms are reported. No physical significance should be attached to the thermal parameters since they are seriously influenced by any systematic errors in the experimental intensities.

The most significant interatomic distances, bond angles, and internal rotation angles are given in Table III. Atoms are numbered according to Figure 1 where a molecular model of $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ projected along the *b* axis is shown.

Description and Discussion of the Molecular Structure

The dimeric molecule formed by two formula units of $(C_5H_5)_2TiAl(C_2H_5)_2$ is linked through a Ti–Ti bond which intersects a twofold symmetry axis. A system of four metal atoms Al–Ti–Ti–Al bonded in sequence is thus observed.

The results of least-square planes calculation show

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[1] G. Natta, G. Mazzanti, P. Corradini, U. Giannini, and S. Cesca, *Atti Accad. Nazl. Lincei, Rend., Classe Sci., Fis., Mat. Nat.*, **26**, 150 (1959).

[2] "International Tables for X-ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959.

[3] J. G. Rollet and R. A. Sparks, *Acta Cryst.*, **13**, 273 (1960).

[4] Unpublished data, but see: G. Natta and P. Corradini, *Angew. Chem.*, **72**, 39 (1960).

[5] For differential synthesis calculations see: A. Damiani, P. De Santis, E. Giglio, and A. Ripamonti, *Ric. Sci., Ser. II-A*, **33**, 965 (1963). Other programs are not published.

[6] The refinement of this structure was carried out on our data by a referee with a full-matrix, least-squares program. The results of this refinement corroborate our structural analysis. The standard deviations on the coordinates listed in Table II come from that least-squares refinement, and they are considerably higher than those estimated from differential synthesis refinement.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (F_{000} = 952)

	h	k	l	F_o	F_c
•	2	0	0	50	37
	4	0	0	121	-120
	6	0	0	126	-135
•	1	1	0	160	188
•	3	1	0	14	10
•	5	1	0	29	-31
	7	1	0	28	-30
•	2	2	0	113	110
•	4	2	0	66	69
	6	2	0	30	40
	8	2	0	31	-32
•	1	3	0	36	34
	3	3	0	15	-22
	5	3	0	67	78
	7	3	0	30	30
	0	4	0	70	60
	2	4	0	35	-50
	6	4	0	54	61
	8	4	0	37	40
	3	5	0	18	-16
	5	5	0	47	46
	7	5	0	44	47
	0	6	0	85	-102
	4	6	0	25	38
	6	6	0	52	53
	1	7	0	70	82
	5	7	0	27	-25
	0	8	0	141	190
	4	8	0	48	-59
	1	9	0	20	17
	5	9	0	17	-17
	0	10	0	69	-74
	4	10	0	40	42
	1	11	0	26	-29
	5	11	0	28	25
	0	12	0	59	-36
	1	13	0	39	-47
	0	14	0	61	-46
	0	16	0	62	56
•	1	1	1	160	-178
•	2	1	1	18	-23
	3	1	1	27	30
	4	1	1	37	29
	5	1	1	107	109
	10	1	1	35	-18
•	0	2	1	159	-227
•	1	2	1	55	56
•	2	2	1	24	21
	3	2	1	99	105
	4	2	1	27	24
	5	2	1	21	21
	6	2	1	62	66
	8	2	1	19	29
	9	2	1	16	-32
•	1	3	1	48	-59
	2	3	1	17	31
	3	3	1	39	-41
	4	3	1	13	20
	5	3	1	27	29
	7	3	1	55	65
	8	3	1	22	-28
•	0	4	1	72	76
•	1	4	1	47	60
	3	4	1	17	18
	4	4	1	15	-10
	5	4	1	17	20
	6	4	1	19	14
•	1	5	1	24	41
	2	5	1	39	-49
	3	5	1	28	31
	4	5	1	31	-38
	5	5	1	17	-21
	7	5	1	27	-22
	8	5	1	18	16
•	0	6	1	86	100
•	1	6	1	36	-43
	2	6	1	36	41
	3	6	1	37	-43
	4	6	1	24	-23
	6	6	1	44	-34
	7	6	1	22	17
	1	7	1	75	90
	5	7	1	39	-54
	3	8	1	22	-24
	4	8	1	20	18
	1	9	1	39	-55
	5	9	1	43	50
	0	10	1	59	-67
	2	11	1	32	28
	2	13	1	37	-29
	2	15	1	39	42
	1	17	1	24	-27
•	2	0	2	54	48
	3	0	2	51	-50
	4	0	2	42	40
	7	0	2	38	44
	8	0	2	16	15
	9	0	2	31	-35
•	1	1	2	78	-88
•	2	1	2	152	146
	3	1	2	18	-16
	4	1	2	50	51
	5	1	2	37	37
	0	2	2	47	53
	1	2	2	112	109
	3	2	2	54	69
	4	2	2	28	-33
	5	2	2	42	-36
	6	2	2	18	20
	7	2	2	40	-51
	8	2	2	15	-23
•	1	3	2	37	40
	2	3	2	14	-19
	4	3	2	81	-94
	5	3	2	45	-47
	7	3	2	20	-23
	8	3	2	21	23
•	0	4	2	120	126
•	1	4	2	35	-41
•	2	4	2	12	17
	3	4	2	124	-151
	4	4	2	19	-15
	5	4	2	30	-43
	6	4	2	60	-67
	7	4	2	40	46
	9	4	2	28	27
•	1	5	2	19	21
	2	5	2	51	-65
	4	5	2	54	-68
	5	5	2	17	-18
	6	5	2	13	-7
	7	5	2	34	-33
	8	5	2	20	21
•	0	6	2	16	-31
•	1	6	2	56	53
	2	6	2	25	-33
	3	6	2	42	49
	4	6	2	23	24
	5	6	2	21	-17
	7	6	2	27	-32
	1	7	2	21	-29
	2	7	2	25	29
	5	7	2	21	22
	0	8	2	83	-96
	5	8	2	18	19
	1	9	2	20	-24
	2	9	2	32	43
	4	9	2	23	24
	6	9	2	20	23
	3	10	2	25	38
	2	11	2	29	-37
	4	11	2	35	-30
	5	11	2	19	-21
	1	12	2	29	-34
	3	12	2	56	-57
	1	13	2	25	21
	2	13	2	33	-21
	1	1	3	14	-8
	2	1	3	34	46
	4	1	3	59	-58
	6	1	3	26	-23
	0	2	3	104	105
	1	2	3	90	-83
	2	2	3	15	-14
	3	2	3	100	-99
	4	2	3	20	-21
	5	2	3	45	-49
	6	2	3	13	-18
	7	2	3	26	26
	9	2	3	44	45
	1	3	3	69	-83
	2	3	3	78	-86
	3	3	3	13	18
	4	3	3	53	-60
	5	3	3	21	-21
	8	3	3	41	44
	9	3	3	27	26
•	0	4	3	17	-38
	1	4	3	36	40
	4	4	3	17	20
	5	4	3	17	18
	6	4	3	15	-17
	1	5	3	81	-83
	2	5	3	99	92
	4	5	3	62	69
	5	5	3	43	42
	7	5	3	20	25
	8	5	3	41	-37
•	0	6	3	116	-127
	1	6	3	59	62
	3	6	3	123	131
	6	6	3	25	27
	9	6	3	35	-29
	2	7	3	27	24
	4	7	3	24	24
	1	8	3	20	24
	1	9	3	20	-21
	4	9	3	29	-20
	1	10	3	33	-52
	3	10	3	51	-48
	5	10	3	25	-25
	1	11	3	18	19
	2	11	3	28	-39
	4	11	3	35	-23
	5	11	3	25	-24
	2	13	3	36	41
	3	14	3	39	37
	0	0	4	144	-140
	1	0	4	223	-181
	2	0	4	154	-147
	3	0	4	111	-116
	4	0	4	72	83
	5	0	4	48	-56
	6	0	4	48	50
	7	0	4	28	30
	9	0	4	39	38
	1	1	4	76	-62
	2	1	4	29	-30
	4	1	4	60	-47
	5	1	4	28	-24
	8	1	4	31	18
	0	2	4	97	-82
	1	2	4	104	86
	2	2	4	29	36
	3	2	4	36	-42
	4	2	4	39	-52
	5	2	4	28	26
	6	2	4	45	-50
	7	2	4	14	-13
	8	2	4	23	23
	10	2	4	22	22
	1	3	4	56	-58
	2	3	4	26	24
	4	3	4	80	84
	8	3	4	31	-34
	0	4	4	109	-96
	1	4	4	10	-9
	3	4	4	85	85
	4	4	4	14	13
	5	4	4	21	23
	9	4	4	38	-40
	1	5	4	37	-32
	2	5	4	62	61
	4	5	4	40	29
	8	5	4	23	-24
	0	6	4	11	25
	1	6	4	29	32
	2	6	4	17	23
	4	6	4	53	-54
	6	6	4	25	-27
	8	6	4	25	-17
	1	7	4	23	-19
	2	7	4	56	-75
	4	7	4	60	-64
	0	8	4	80	-67
	1	8	4	59	-65
	2	8	4	27	-38
	3	8	4	75	-78
	4	8	4	60	50
	2	9	4	49	-50
	4	9	4	47	-46
	4	10	4	22	-16
	2	11	4	29	23
	4	11	4	29	26
	3	12	4	41	30
	2	13	4	32	33
	1	1	5	95	75
	2	1	5	55	55
	4	1	5	94	83
	5	1	5	79	-76
	6	1	5	29	-26
	7	1	5	31	-31
	8	1	5	33	-33
	0	2	5	48	-27
	1	2	5	25	17
	2	2	5	66	70
	3	2	5	81	73
	4	2	5	31	-29
	5	2	5	25	31
	6	2	5	28	-26
	8	2	5	26	-27
	9	2	5	36	-33
	1	3	5	25	-29
	2	3	5	21	28
	3	3	5	20	-18
	4	3	5	55	53
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	6	3	5	29	28
	7	3	5	20	-11
	8	3	5	21	-15
	9	3	5	22	-19
	0	4	5	14	1
	1	4	5	28	-29
	2	4	5	18	-22
	1	5	5	64	-60
	4	5	5	27	-22
	5	5	5	11	-8
	6	5	5	17	-19
	7	5	5	14	13
	8	5	5	22	22
	9	5	5	15	17
	0	6	5	71	-67
	1	6	5	50	-56
	2	6	5	36	-32
	3	6	5	71	-63
	6	6	5	20	21
	9	6	5	26	24
	1	7	5	84	-91
	2	7	5	83	-92
	4	7	5	29	-25
	5	7	5	48	56
	1	8	5	16	-15
	2	8	5	21	-16
	1	9	5	27	46
	2	9	5	46	51
	4	9	5	51	54
	5	9	5	40	-45
	1	10	5	25	27
	3	10	5	48	50
	4	10	5	22	-16
	4	11	5	30	23
	1	12	5	29	-22
	1	0	6	70	66
	2	0	6	68	68
	3	0	6	177	155
	6	0	6	32	-35
	7	0	6	23	-29
	9	0	6	40	-42
	1	1	6	105	83
	4	1	6	78	70
	5	1	6	33	-38
	0	2	6	36	23
	1	2	6	59	-50
	2	2	6	12	14
	3	2	6	19	-24
	4	2	6	35	-31
	5	2	6	26	25
	6	2	6	20	23
	7	2	6	18	18
	8	2	6	16	20
	1	3	6	41	-44
	2	3	6	31	34
	4	3	6	20	-20
	5	3	6	37	37
	7	3	6	35	42
	8	3	6	29	14
	0	4	6	127	-121
	2	4	6	60	-57
	3	4	6	15	-14
	4	4	6	66	65
	6	4	6	51	49
	8	4	6	30	32
	1	5	6	33	-39
	2	5	6	37	-36
	5	5	6	25	24
	7	5	6	33	32
	0	6	6	41	36
	1	6	6	46	-49
	3	6	6	38	-34
	4	6	6	16	-17
	5	6	6	23	21
	7	6	6	21	21
	1	7	6	78	42
	4	7	6	30	19
	5	7	6	18	-20
	0	8	6	64	68
	1	8	6	54	69
	2	8	6	46	47
	3	8	6	74	71
	4	8	6	22	-20
	1	9	6	27	37
	5	9	6	22	-25
	1	10	6	32	-44
	1	11	6	23	-30
	0	12	6	61	-51
	2	1	7	64	-58
	3	1	7	50	-54
	4	1	7	41	-48
	5	1	7	29	28
	6	1	7	28	29
	7	1	7	37	30
	8	1	7	32	22
	0	2	7	76	-103
	2	2	7	59	-50
	3	2	7	21	-20
	4	2	7	48	48
	6	2	7	66	69
	7	2	7	18	-18
	8	2	7	27	23
	1	3	7	100	-88
	2	3	7	35	36
	3	3	7	31	31
	5	3	7	59	57
	6	3	7	20	-16
	7	3	7	28	33
	0	4	7	80	90
	1	4	7	33	-26
	3	4	7	40	-43
	4	4	7	17	21
	1	5	7	146	127
	2	5	7	65	-68
	3	5	7	28	-29
	5	5	7	47	-32
	7	5	7	20	-23
	0	6	7	117	112
	2	6	7	80	78
	4	6	7	47	-47
	6	6	7	28	-23
	8	6	7	25	-25
	1	7	7	39	42
	2	7	7	45	55
	3	7	7	27	27
	1	8	7	20	-21
	2	9	7	40	-43
	0	10	7	61	-45
	5	10	7	17	14
	1	11	7	23	-27
	0	12	7	53	34
	1	13	7	32	46
	0	0	8	137	-105
	2	0	8	51	-49
	3	0	8	80	86
	6	0	8	54	50
	7	0	8	24	-21
	8	0	8	25	-33
	1	1	8	90	-71
	2	1	8	71	57
	4	1	8	13	18
	5	1	8	48	55
	7	1	8	33	21
	0	2	8	65	-59
	1	2	8	15	15
	2	2	8	60	-46
	3	2	8	10	-13
	4	2	8	60	61
	5	2	8	13	16
	1	3	8	71	69
	2	3	8	55	-49
	5	3	8	46	-45
	7	3	8	27	-30
	0	4	8	123	112
	1	4	8	19	-25
	2	4	8	63	61
	3	4	8	18	29
	4	4	8	80	-69
	5	4	8	24	-21
	6	4	8	37	-36
	8	4	8	27	-23
	1	5	8	56	54
	4	5	8	16	-10
	5	5	8	28	-31
	7	5	8	33	-33
	0	6	8	20	-29
	4	6	8	42	35
	1	7	8	43	-45
	2	7	8	22	26
	5	7	8	33	26
	5	8	8	25	25
	1	9	8	22	-32
	5	9	8	29	25
	4	10	8	27	15
	1	11	8	28	28
	1	13	8	30	25
	0	14	8	64	-33
	1	17	8	31	-15
	2	1	9	121	-100
	3	1	9	47	48
	4	1	9	55	-53
	6	1	9	35	22
	0	2	9	126	110
	1	2	9	48	-42
	2	2	9	40	28
	3	2	9	73	-70
	4	2	9	50	-49
	5	2	9	38	-37
	6	2	9	36	-32
	7	2	9	24	17
	8	2	9	20	-19
	9	2	9	18	15
	1	3	9	100	87
	3	3	9	21	-22
	4	3	9	17	-16
	5	3	9	37	-40
	6	3	9	30	-26
	7	3	9	28	-27
	5	4	9	25	-35
	1	5	9	36	-49
	2	5	9	30	27
	3	5	9	19	20
	4	5	9	18	-21
	5	5	9	37	28
	0	6	9	46	-47
	1	6	9	30	41
	2	6	9	40	-34
	3	6	9	17	10
	4	6	9	28	22
	5	6	9	25	20
	6	6	9	30	30
	7	6	9	25	-20
	1	7	9	47	22
	2	7	9	44	50
	3	7	9	29	-30
	4	7	9	32	27
	2	9	9	37	-36
	4	9	9	54	-43
	0	10	9	66	54
	1	10	9	24	-21
	1	11	9	25	28
	1	13	9	22	-25
	0	0	10	70	44
	1	0	10	154	-112
	3	0	10	135	-123
	4	0	10	23	-17
	5	0	10	46	-41
	7	0	10	64	63
	1	1	10	39	36
	2	1	10	103	-84
	4	1	10	57	-52
	5	1	10	17	-13
	6	1	10	19	-6
	2	2	10	17	-16
	3	2	10	11	14
	4	2	10	16	12
	7	2	10	24	-26
	1	3	10	16	-18
	2	3	10	42	39
	4	3	10	17	12
	5	3	10	28	27
	0	4	10	13	-14
	1	4	10	23	27
	3	4	10	32	36
	4	4	10	22	15
	5	4	10	32	30
	1	5	10	11	-14
	2	5	10	20	19
	4	5	10	29	30
	8	5	10	17	-18
	0	6	10	21	24
	7	6	10	25	-20
	2	7	10	24	-24
	1	8	10	39	-40
	3	8	10	71	-59
	5	8	10	27	-28
	1	1	11	41	-28
	2	1	11	96	89
	4	1	11	59	64
	5	1	11	39	41
	0	2	11	40	-27
	1	2	11	66	60
	3	2	11	51	46
	5	2	11	39	40
	6	2	11	15	-19
	7	2	11	23	-19
	1	3	11	44	42
	2	3	11	41	37
	4	3	11	21	13
	5	3	11	44	-48
	6	3	11	20	20
	1	5	11	32	-36
	2	5	11	41	-41
	4	5	11	20	-13
	5	5	11	14	14
	0	6	11	37	-36
	3	6	11	58	-55
	5	6	11	25	-22
	2	7	11	49	-47
	4	7	11	53	-50
	5	7	11	31	-34
	1	9	11	26	-31
	2	9	11	37	35
	0	10	11	54	-13
	1	10	11	27	27
	1	13	11	28	-25
	1	0	12	79	68
	2	0	12	49	43
	3	0	12	25	36
	4	0	12	20	11
	5	0	12	42	36
	7	0	12	32	-28
	1	1	12	49	50
	2	1	12	32	27
	0	2	12	88	84
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	5	2	12	25	-18
	1	3	12	18	-16
	2	3	12	51	-44
	4	3	12	40	-44
	7	3	12	44	25
	0	4	12	35	-44
	1	4	12	40	-37
	2	4	12	19	-18
	3	4	12	76	-69
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	5	4	12	26	-22
	6	4	12	40	45
	6	6	12	25	-15
	1	7	12	23	27
	2	7	12	36	35
	1	5	12	19	-22
	2	5	12	20	-20
	4	5	12	29	-28
	5	5	12	15	21
	0	6	12	27	23
	4	7	12	26	18
	3	8	12	27	27
	1	9	12	20	18
	2	1	13	31	27
	0	2	13	48	-58
	1	2	13	32	-30
	2	2	13	42	-42
	3	2	13	21	-25
	4	2	13	20	22
	6	2	13	46	46
	1	3	13	25	-37
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	4	3	13	21	-13
	5	3	13	31	24
	7	3	13	23	16
	8	3	13	31	20
	2	4	13	14	13
	3	4	13	15	20
	1	5	13	48	49
	2	5	13	57	60
	4	5	13	23	24
	5	5	13	26	-27
	0	6	13	67	64
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	3	6	13	30	24
	4	6	13	22	-20
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	6	6	13	32	-30
	1	7	13	19	19
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	7	3	14	26	-23
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	3	6	14	25	-26
	1	7	14	24	-30
	1	9	14	26	-29
	1	11	14	27	24
	1	1	15	58	68
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	2	2	15	32	33
	6	2	15	41	-39
	3	4	15	23	21
	4	5	15	15	18
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	2	6	15	29	-31
	3	6	15	24	16
	4	6	15	28	27
	6	6	15	27	16
	1	7	15	50	-43
	2	7	15	27	31
	1	9	15	30	43
	0	0	16	90	86
	2	0	16	36	41
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	1	4	18	19	-22
	3	4	18	58	-57
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	0	0	20	84	-70
	2	0	20	31	-35
	3	0	20	34	-34
	4	0	20	28	30
	6	0	20	30	32
	0	6	20	25	19
	0	6	21	28	-32

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS

	x/a	$\sigma(x)$, A	y/b	$\sigma(y)$, A	z/c	$\sigma(z)$, A	B, A^2
Ti	0.0813	0.0055	0.1252	0.0059	0.3196	0.0046	
Al	0.1062	0.0094	0.2510	0.0101	0.1228	0.0082	
C(1)	0.4998	0.034	0.4720	0.034	0.3330	0.034	4.24
C(2)	0.0474	0.031	0.0265	0.031	0.1082	0.030	4.94
C(3)	0.0776	0.033	0.0587	0.032	0.4308	0.030	4.17
C(4)	0.1908	0.035	0.0240	0.040	0.3969	0.037	5.18
C(5)	0.3592	0.030	0.4726	0.032	0.3337	0.031	5.00
C(6)	0.1432	0.026	0.1801	0.030	0.2156	0.027	3.76
C(7)	0.1667	0.029	0.2558	0.035	0.2631	0.030	3.16
C(8)	0.2830	0.027	0.2320	0.031	0.3065	0.028	3.54
C(9)	0.3181	0.031	0.1438	0.036	0.2886	0.030	4.54
C(10)	0.2465	0.032	0.1146	0.034	0.2306	0.026	4.49
C(11)′	0.0996	0.035	0.3802	0.032	0.1331	0.027	3.48
C(12)′	0.0714	0.040	0.4340	0.040	0.0681	0.038	6.40
C(13)′	0.2517	0.036	0.2140	0.040	0.0450	0.031	3.48
C(14)′	0.3990	0.043	0.2392	0.040	0.0741	0.038	5.72

Anisotropic Thermal Parameters

$$\exp[-(h^2\beta_{11} + hk\beta_{12} + hl\beta_{13} + k^2\beta_{22} + kl\beta_{22} + l^2\beta_{33})$$

	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Ti	0.0061	0.0042	0.0025	0.0027	0.0022	0.0008
Al	0.0061	0.0039	0.0026	0.0026	0.0025	0.0012

	x/a	y/b	z/c	X[a]		x/a	y/b	z/c	X[a]
H(1)	−0.065	−0.060	0.295	C(1)	H(11)	0.014	0.398	0.169	C(11)′
H(2)	−0.158	0.043	0.404	C(2)	H(12)	0.201	0.406	0.153	C(11)′
H(3)	0.079	0.101	0.478	C(3)	H(13)	0.067	0.509	0.046	C(12)′
H(4)	0.303	0.034	0.412	C(4)	H(14)	0.972	0.414	0.046	C(12)′
H(5)	0.210	−0.060	0.295	C(5)	H(15)	0.159	0.418	0.031	C(12)′
H(6)	0.063	0.175	0.175	C(6)	H(16)	0.243	0.141	0.033	C(13)′
H(7)	0.111	0.321	0.267	C(7)	H(17)	0.229	0.252	0.997	C(13)′
H(8)	0.333	0.270	0.349	C(8)	H(18)	0.417	0.199	0.120	C(14)′
H(9)	0.404	0.106	0.316	C(9)	H(19)	0.405	0.308	0.086	C(14)′
H(10)	0.260	0.046	0.205	C(10)	H(20)	0.472	0.218	0.034	C(14)′

[a] X is carbon atom bonded to H.

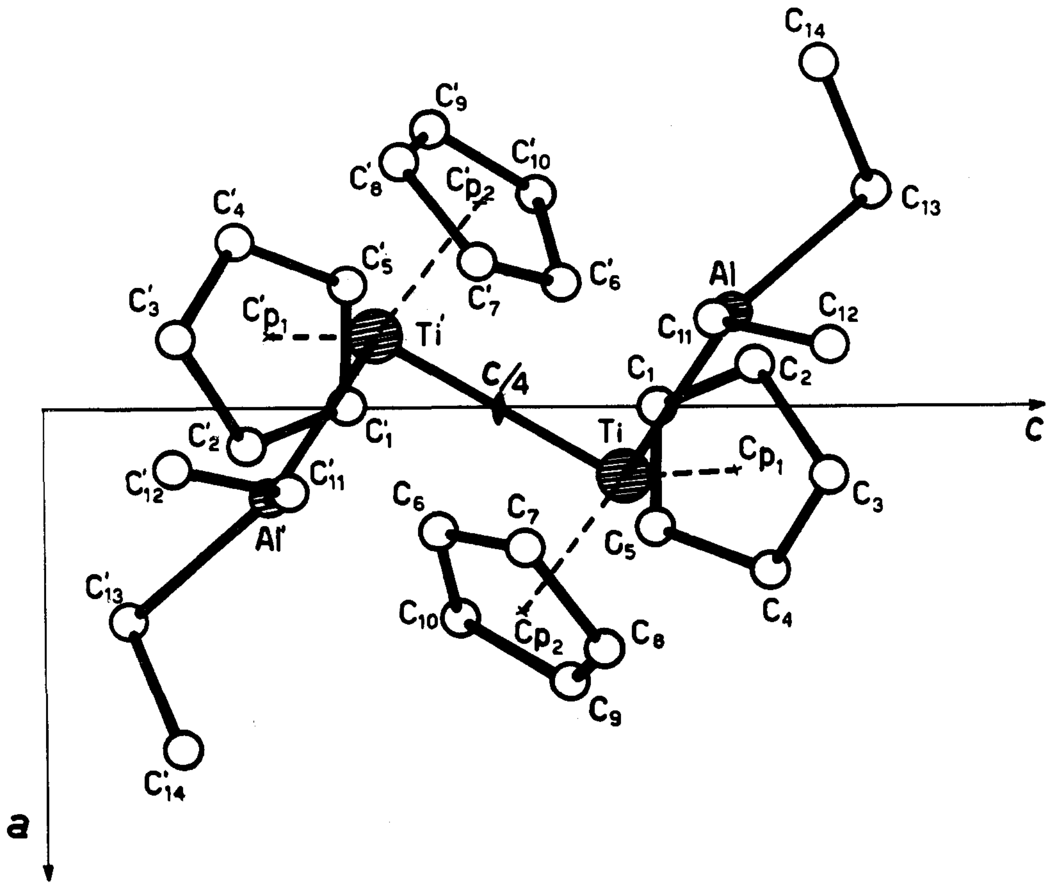

Figure 1.—[010] projection of the molecule.

TABLE III

BOND LENGTHS, BOND ANGLES, AND RELATIVE STANDARD DEVIATIONS

	Bond, A	Dev, A		Angle, deg	Dev, deg
Ti-Ti	3.110	0.007	Ti'TiAl	91.8	0.3
Ti-Al	2.792	0.011	Cp_1TiCp_2	136.2	
C(1)-C(2)	1.45	0.04	C(1)C(2)C(3)	108.4	2.6
C(2)-C(3)	1.48	0.04	C(2)C(3)C(4)	106.0	2.7
C(3)-C(4)	1.36	0.05	C(3)C(4)C(5)	109.0	2.9
C(4)-C(5)	1.51	0.05	C(4)C(5)C(1)	108.3	2.8
C(5)-C(1)	1.34	0.04	C(5)C(1)C(2)	108.0	2.8
Ti-C(1)	2.37	0.03			
Ti-C(2)	2.34	0.03			
Ti-C(3)	2.37	0.03			
Ti-C(4)	2.35	0.04			
Ti-C(5)	2.31	0.03			
$Ti-Cp_1$	2.01				
C(6)-C(7)	1.46	0.04	C(6)C(7)C(8)	107.8	2.7
C(7)-C(8)	1.43	0.04	C(7)C(8)C(9)	105.4	2.6
C(8)-C(9)	1.37	0.05	C(8)C(9)C(10)	112.0	2.8
C(9)-C(10)	1.38	0.04	C(9)C(10)C(6)	107.6	2.8
C(10)-C(6)	1.40	0.04	C(10)C(6)C(7)	106.2	2.4
Ti-C(6)	2.25	0.03	TiAlC(11)	126.5	1.0
Ti-C(7)	2.35	0.03	TiAlC(13)	122.3	1.0
Ti-C(8)	2.48	0.03	TiC(6)'Al	77.0	1.4
Ti-C(9)	2.34	0.03	C(11)AlC(13)	110.0	1.4
Ti-C(10)	2.34	0.03	C(6)'AlC(13)	112.0	1.3
			C(6)'AlC(11)	114.4	1.4
$Ti-Cp_2$	2.02		AlC(11)C(12)	116.8	2.2
Ti-C(6)'	2.38	0.03	AlC(13)C(14)	105.7	2.3
Al-C(11)	1.89	0.03	Al'Ti'TiTi'TiAl	97.7	0.5
C(11)-C(12)	1.50	0.05			
Al-C(13)	2.11	0.03			
C(13)-C(14)	1.55	0.05			
Al-C(6)	2.11	0.03			

that both cyclopentadienyl rings (which are indicated together with their center as Cp_1 and Cp_2) are essentially planar.

The calculated least-square planes are $X + 19.639Y - 13.040Z + 91.641 = 0$ for Cp_1 with a maximum deviation of 0.029 A for C(5) and $X + 0.6213Y - 0.9688Z + 1.0249 = 0$ for Cp_2 with a maximum deviation of 0.046 A for C(10).

Although a lack of fivefold symmetry is indicated for Cp_1, the differences between carbon–carbon bond lengths are on the borderline of statistical significance.

The $Ti-Cp_1$ axis is normal to the plane containing the cyclopentadienyl ring. The carbon–carbon bond lengths found for the Cp_2 ring are all equal within the errors. However, the observable differences between Ti–C bond distances (see Table III) appear significant. The $Ti-Cp_2$ axis makes an angle of 8° with the normal to the plane containing the ring. The direction of the observed distortion in favor of a positioning of C(6) closer to the Ti'–Al' bond is consistent with some other structural features peculiar to this compound as discussed below.

The coordination around the Al atom is particularly interesting. Atoms C(11), C(13), and Ti are trigonally disposed around Al (with angles C(11)AlC(13) = 110.0°, C(11)AlTi = 126.5°, and C(13)AlTi = 122.3°) which departs from the plane of the former three by 0.12 A in the direction of C(6)'. On the other hand, quite short distances occur between Al and C(6)' and Ti and C(6)'; the Al–C(6)', distance of 2.11 A closely

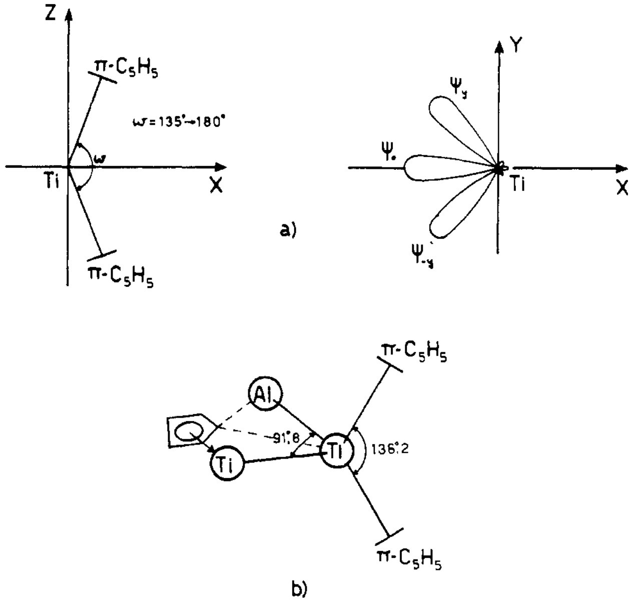

Figure 2.—Coordination around the Ti atom: (a) theoretical model;[6] (b) scheme of the coordination actually found.

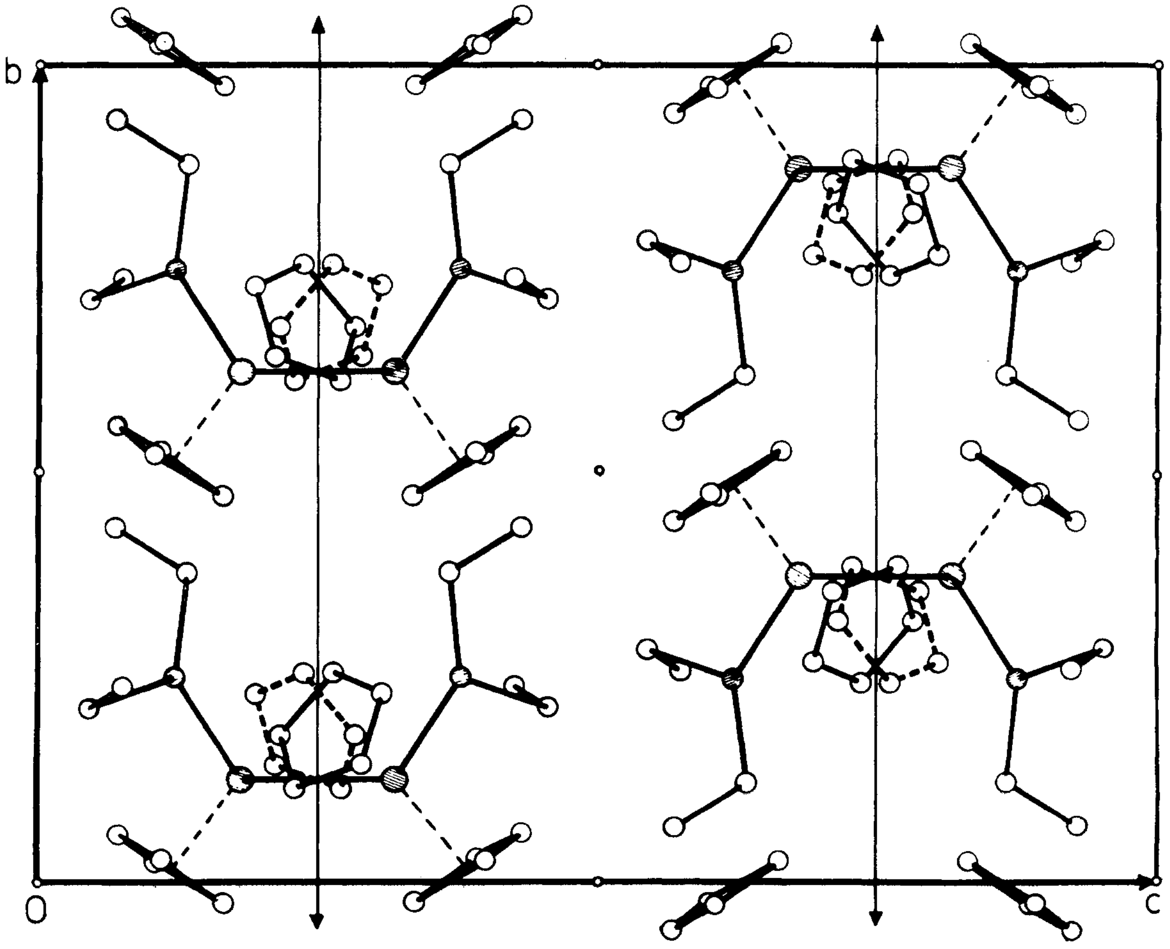

Figure 3.—[100] projection of the content of the unit cell.

corresponds to a σ Al–C bond length while the Ti–C(6)′ distance of 2.38 A is practically equal to the mean Ti–C distance found in the Ti–Cp$_1$ system. The TiC(6)′Al angle is 77.0°, typical of a bridging carbon atom.

The coordination around each Ti atom together with the over-all structure of the molecule may be understood on the basis of the theoretical model proposed by Ballhausen and Dahl[7] for protonated sandwhich compounds or for such compounds as $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$.[8]

Figure 2 shows schematically the proposed model (a) and how it applies to the present case (b). It is assumed, therefore, that ψ_y and ψ_{-y} are utilized for bonding with a Ti and an Al atom. Moreover, a bridge could be formed between Al and Ti through the interaction of an appropriate filled Cp$_2$ ring orbital both with the empty ψ_0 Ti orbital and an empty Al orbital of prevailing p character. This additional bonding function of the Cp$_2$ rings justifies the above referred distortion of the plane of the ring with respect to the Ti–Cp$_2$ axis. It also explains a departure from the theoretical dihedral angle between the planes containing the Al–Ti–Ti′ and Cp$_1$–Ti–Cp$_2$ systems which should be 90°. The observed angle is 75°. This distortion appears to be a consequence of the translation of the Cp$_2$ ring toward the ψ_0 Ti orbital.

An alternative description of the structure in terms of valence bonds involving resonance among extreme forms is schematically shown below.

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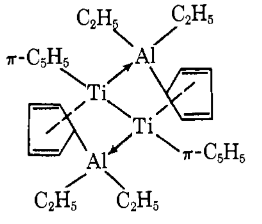
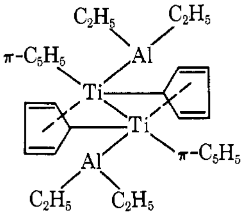
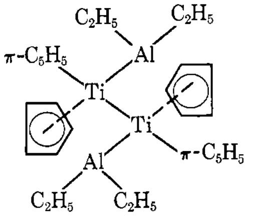

I


II


III

All three resonance forms are consistent with the diamagnetism of the compound. Forms I and II show clearly the half-bridge nature of the bonding between Ti and Al. Form I involves some Lewis basicity of the Ti atoms toward the Al atoms. This was suggested in the earlier study of this compound.[3] Recently, other examples of Lewis basicity of metals have been reported.[9–11]

The Crystal Structure

Figure 3 shows the content of the unit cell projected on the *bc* plane. Ethyl groups and cyclopentadienyl rings clustered about axes parallel to the *a* axis and containing centers of symmetry exhibit the closest packing distances. Minimum carbon–carbon distances of 3.52 A between centrosymmetrically related methyl groups and of 3.48 A for similarly related cyclopentadienyl rings are observed. No H–H contact distances less than 2.24 A have been calculated with the hydrogen atoms in the positions listed in Table II.

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[10] G. W. Parshall, *ibid.*, **86**, 361 (1964).

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X-Ray Analyses of the Structures of Two Crystalline Forms of *trans*-Dichlorotetrakis(ethylenethiourea)nickel(II)[1]

BY WARD T. ROBINSON,[2] SMITH L. HOLT, JR., AND GENE B. CARPENTER

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trans-Dichlorotetrakis(ethylenethiourea)nickel(II), $Ni[SC(NHCH_2)_2]_4Cl_2$, is polymorphous, crystallizing in the triclinic system with one molecule in the unit cell (space group $P\bar{1}$) and in the monoclinic system with four molecules in the unit cell (space group $C2/c$). Both structures have the same NiS_4 skeleton, including two unequal independent Ni–S bonds, but differ in the orientation and length of the Ni–Cl bonds and also in the orientation of the ethylenethiourea ligands. There is no clear evidence for intermolecular or intramolecular hydrogen bonding in these crystals.

Introduction

The structure of dichlorotetrakis(ethylenethiourea)nickel(II) $[Ni(etu)_4Cl_2]$ was first investigated by Nardelli, Chierici, and Braibanti.[3] Weissenberg photographs were obtained by rotating small yellow crystals about the z axis. Crystallographic data were reported as $a = 8.42$, $b = 8.44$, $c = 8.82$ A; $\alpha = 107.0°$, $\beta = 117.5°$, $\gamma = 90.2°$; $V = 524$ A^3; $Z = 1$; $D_m = 1.67$; $D_c = 1.70$. A qualitative comparison of $hk0$ Weissenberg photographs[4] from this crystal and from the corresponding thiourea complex,[5] $[Ni(tu)_4Cl_2]$, led these authors to deduce that there must be marked structural analogies between the compounds. In particular they concluded that the coordination of the four sulfur atoms of the ethylenethiourea molecules around the nickel atom must take place in one plane, chlorine atoms completing an octahedron in *trans* positions. This conclusion has, essentially, been confirmed by the present work.

Both yellow and orange crystalline forms of $[Ni(etu)_4Cl_2]$ were subsequently studied by Holt and Carlin.[6] The yellow form was assumed to be identical with the compound reported by Nardelli, *et al.*, and their conclusion that this was a *trans* complex was accepted. Indeed this conclusion was further supported by an examination of reflectance spectra. The splitting of spectral bands of the yellow compound was observed to be twice that of the orange compound, and it had been shown theoretically and experimentally

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[1] Research supported by Advanced Research Projects Agency Contract SD-86.

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