Crystal and Molecular Structure of Two Seven-co-ordinate Distorted Pentagonal Bipyramidal Complexes of Tantalum(v)

By **Michael G. B. Drew,*** Department of Chemistry, The University, Whiteknights, Reading RG6 2AD
John D. Wilkins, Department of Chemistry, University College, London WC1H 0AJ

Crystals of (I) $[TaCl_3L^1_2]$ (L^1 = *NN'*-dicyclohexylacetamidinate) are tetragonal, space group $I\bar{4}$, with cell dimensions: a = 26.328(9), c = 10.368(5) Å, Z = 8. Crystals of (II) $[TaCl_3L^1L^2]$ [L^2 = (probably) *NN'*-dicyclohexylureate] are monoclinic, space group *Cc* with cell dimensions a = 12.209(8), b = 23.464(15), c = 12.324(11) Å, β = 115.34(9)°, Z = 4. Both structures were solved by Patterson and Fourier methods from diffractometer data and refined by least-squares methods to R 0.075 [(I), 2 017 reflections] and 0.060 [(II), 2 232 independent reflections]. They are both distorted pentagonal bipyramidal structures with two of the chlorine atoms in axial positions and the other equatorial. The two bidentate ligands complete the pentagonal girdle.

WE have been investigating the structures of a number of compounds of general formula $[Me_nTaCl_{3-n}L_2]$ ($n = 0$ or 1, and L = bidentate acetamidinate). Most structures in this series (namely with $n = 0$,[1,2] or 1,[3] and $L = Pr^iNC(Me)NPr^i$) are distorted pentagonal bipyramids (= P.B.) with two chlorine atoms in axial positions. The exception is the complex with $n = 1$ and $L = C_6H_{11}NC(Me)NC_6H_{11}$ in which the two bidentate ligands are mutually perpendicular and the molecular geometry cannot be directly related to any of the three ideal polyhedra.[4] We therefore decided to determine the structure of $[TaCl_3\{C_6H_{11}NC(Me)C_6H_{11}\}_2]$, (I). Crystals of this compound were prepared and the structure obtained but not before we had carried out a structure determination on a related compound of formula $[TaCl_3\{C_6H_{11}NC(Me)NC_6H_{11}\}\{C_6H_{11}NC(NHC_6H_{11})O\}]$, (II). Both structure determinations are reported here.

EXPERIMENTAL

$[MeTaCl_3\{C_6H_{11}NC(Me)NC_6H_{11}\}]$ (1.91 g) prepared by the literature method [5] was allowed to react with *NN'*-dicyclohexylcarbodi-imide (5.0 g) in dichloromethane (30 cm^3).

---

[1] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1974, 1579.

[2] M. G. B. Drew and J. D. Wilkins, *Acta Cryst.*, 1975, **B31**, 177.

[3] M. G. B. Drew and J. D. Wilkins, *Acta Cryst.*, 1975, in the press.

[4] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1974, 1973.

[5] J. D. Wilkins, *J. Organometallic Chem.*, 1974, **80**, 349.

After 4 days at room temperature, solvent was removed *in vacuo* and the residual orange solid extracted with pentane for several hours to remove excess of carbodi-imide. The light orange powdered solid was pumped dry [Found: Ta, 24.3; Cl, 14.90. Calc. for (I): Ta, 24.85; Cl, 14.60%]. I.r. ν(C⁚N): 1 528ms, 1533, and 1 598s cm^{-1}. The complex did not show ν(N⁚C⁚N). N.m.r. τ(C–Me) 7.65 in CH_2Cl_2 solution.

The powdered material was dissolved in ligroin–CH_2Cl_2 (50:50, v/v). When the solution was allowed to evaporate a very small amount of crystalline material was obtained which was subsequently identified as (II). Further batches of the powdered material were then prepared and under similar conditions a large amount of crystalline material was obtained, which was identified as (I). We were not able to repeat our preparation of (II). The powdered material from all preparations appeared to be identical.

TABLE 1

Positional parameters for (I) ($\times 10^4$), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ta	2 823(1)	0 994(1)	2 878(1)
Cl(1)	2 220(3)	0 975(3)	4 577(9)
Cl(2)	3 450(3)	1 086(3)	1 252(9)
Cl(3)	3 198(3)	1 735(3)	3 912(11)
N(1)	3 439(8)	0 645(7)	3 949(24)
N(2)	2 839(8)	0 176(7)	3 030(25)
N(3)	2 360(9)	0 851(8)	1 281(21)
N(4)	2 334(7)	1 594(9)	2 194(28)
C(1)	3 281(13)	0 166(11)	3 781(34)
C(2)	3 502(15)	−0 307(11)	4 378(46)
C(3)	2 134(11)	1 303(12)	1 270(34)
C(4)	1 729(11)	1 467(14)	0 260(39)
C(11)	3 939(16)	0 793(15)	4 554(38)
C(12)	3 912(13)	0 774(13)	6 040(36)
C(13)	4 406(15)	1 003(17)	6 592(47)
C(14)	4 897(14)	0 827(14)	5 865(53)
C(15)	4 880(14)	0 880(17)	4 434(45)
C(16)	4 369(13)	0 613(20)	3 929(56)
C(21)	2 432(10)	−0 210(10)	2 994(30)
C(22)	2 253(13)	−0 350(12)	4 320(34)
C(23)	1 786(15)	−0 705(16)	4 140(49)
C(24)	1 932(22)	−1 133(21)	3 163(70)
C(25)	2 167(13)	−1 047(13)	2 074(42)
C(26)	2 578(12)	−0 672(15)	2 226(44)
C(31)	2 349(13)	0 454(16)	0 200(40)
C(32)	2 562(11)	0 603(16)	−1 035(39)
C(33)	2 617(17)	0 209(15)	−2 087(47)
C(34)	2 140(21)	−0 035(15)	−2 300(40)
C(35)	1 884(19)	−0 210(16)	−0 983(41)
C(36)	1 815(12)	0 171(14)	−0 016(34)
C(41)	2 179(11)	2 103(9)	2 514(36)
C(42)	2 371(12)	2 516(13)	1 695(39)
C(43)	2 280(19)	3 017(13)	2 365(54)
C(44)	1 737(16)	3 103(14)	2 561(42)
C(45)	1 509(14)	2 662(13)	3 493(39)
C(46)	1 607(12)	2 128(12)	2 736(64)
H(11) *	3 971	1 197	4 317
H(21)	2 115	−0 042	2 505
H(31)	2 615	0 190	0 641
H(41)	2 370	2 144	3 483

* Parameters fixed for all hydrogen atoms.

Crystal Data.—(*a*), (I). $C_{28}H_{50}Cl_3N_4Ta$, $M = 729.72$, Tetragonal, $a = 26.328(9)$, $c = 10.368(5)$ Å, $D_m = 1.36(2)$, $Z = 8$, $D_c = 1.35$, $U = 7\ 186.7$ Å, $F(000) = 2\ 968$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) $= 33.4$ cm^{-1}. Space group $I\bar{4}$ from systematic absences: *hkl*, $h + k + l = 2n + 1$ and successful structure determination.

(*b*), (II). $C_{27}H_{48}Cl_3N_4TaO$, $M = 729.70$, Monoclinic, $a = 12.209(8)$, $b = 23.464(15)$, $c = 12.324(11)$ Å, $\beta = 115.34(9)°$, $U = 3\ 190.3$ Å^3, $D_c = 1.51$ *, $Z = 4$, $F(000) = 1\ 484$. Mo-K_α radiation, μ(Mo-K_α) $= 36.9$ cm^{-1}. Space group *Cc* from systematic absences: *hkl*, $h + k = 2n + 1$, *h*0*l*, $l = 2n + 1$, and successful structure determination.

A General Electric XRD 5 apparatus was used for measuring cell dimensions *via* least-squares refinement of high-angle reflections and diffraction intensities by the stationary-crystal–stationary-counter method. It was equipped with manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflections which were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. For (I) a crystal *ca.* 0.45 × 0.20 × 1.25 mm was mounted with the *c* axis parallel to the instrument axis. Of 2 504 independent reflections measured with $2\theta < 45°$, 2 017 having $I > \sigma(I)$ were used in subsequent calculations. For (II) a crystal *ca.* 0.2 × 0.15 × 0.80 mm was mounted with the c^* axis parallel to the instrument axis. Of 2 786 independent reflections measured with $2\theta < 50°$, 2 232 had $I > \sigma(I)$ and were used in subsequent calculations.

TABLE 2

Anisotropic thermal parameters ($\times 10^3$) for (I), with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	46.7(8)	34.6(7)	52.1(7)	02.9(6)	−12.3(7)	02.1(7)
Cl(1)	84(6)	64(6)	65(6)	06(5)	15(5)	−12(5)
Cl(2)	52(5)	92(6)	61(6)	−15(4)	−00(4)	14(5)
Cl(3)	74(6)	45(5)	106(8)	02(4)	−29(6)	−14(5)
N(1)	57(14)	27(11)	52(16)	01(10)	−08(12)	−07(12)
N(2)	55(13)	36(11)	53(15)	−03(10)	−24(14)	01(12)
N(3)	81(18)	32(12)	33(14)	24(11)	−26(13)	−15(11)
N(4)	27(11)	80(17)	55(15)	09(11)	−13(14)	29(16)
C(1)	93(26)	39(18)	58(21)	17(17)	07(20)	−07(17)
C(2)	88(25)	27(16)	129(38)	02(15)	−22(26)	27(19)
C(3)	53(19)	67(22)	57(22)	02(16)	−10(18)	−04(19)
C(4)	43(18)	88(26)	99(30)	06(17)	−22(20)	46(24)
C(11)	125(32)	07(13)	86(27)	06(20)	−15(24)	−03(15)
C(12)	79(24)	64(21)	60(23)	−08(18)	−17(20)	01(18)
C(13)	67(25)	112(33)	122(41)	−02(22)	−52(26)	−19(29)
C(14)	56(23)	68(24)	152(49)	−03(18)	−23(27)	−37(28)
C(15)	59(23)	114(33)	81(31)	−12(21)	02(22)	−22(26)
C(16)	34(19)	175(46)	146(45)	69(25)	−14(25)	−22(39)
C(21)	50(16)	55(16)	34(16)	16(13)	−15(16)	−11(16)
C(22)	71(22)	68(21)	59(23)	−28(18)	−21(19)	26(18)
C(23)	59(23)	92(30)	120(38)	01(21)	−03(25)	13(28)
C(24)	107(41)	78(32)	392(127)	−29(29)	74(67)	17(59)
C(25)	57(22)	88(26)	71(25)	−07(19)	04(25)	−15(28)
C(26)	58(20)	118(31)	69(25)	10(20)	−10(22)	38(28)
C(31)	68(24)	110(31)	73(27)	36(22)	−14(22)	10(24)
C(32)	37(18)	117(31)	88(30)	−15(18)	07(19)	62(26)
C(33)	132(27)	87(26)	76(27)	−16(25)	−56(31)	−31(27)
C(34)	172(45)	73(25)	48(24)	22(25)	−09(27)	−20(21)
C(35)	164(45)	106(31)	69(29)	−77(33)	−31(30)	−29(26)
C(36)	47(19)	86(25)	63(23)	−25(17)	−27(17)	−00(20)
C(41)	71(20)	19(13)	107(36)	−06(13)	07(19)	−11(16)
C(42)	67(23)	52(19)	107(36)	02(17)	06(21)	07(20)
C(43)	159(42)	43(20)	165(55)	−43(24)	78(40)	09(26)
C(44)	106(30)	79(26)	108(41)	57(23)	31(26)	−20(24)
C(45)	78(24)	62(21)	76(25)	−04(18)	−16(21)	05(20)
C(46)	42(18)	51(19)	249(63)	06(14)	38(30)	−06(32)

Standard reflections were monitored during data collection from (I) and (II) but no significant changes in intensity were observed. For both crystals, absorption corrections were applied by use of the program ABSORB [6]

* D_m for crystals was not measured. D_m for the powdered material was 1.36. For (I) D_m for crystals was measured.

[6] '*X*-Ray' system of programs, ed. J. M. Stewart, University of Maryland Technical Report TR 194, July, 1970.

which uses the Gaussian quadrature method; transmission factors varied between 0.39 and 0.47 for (I) and 0.46 and 0.58 for (II). No extinction corrections were applied.

TABLE 3

Positional co-ordinates ($\times 10^4$) for (II), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ta	0 000 [a]	1 346(1)	2 500 [a]
Cl(1)	−0 592(7)	0 985(3)	0 513(7)
Cl(2)	0 451(8)	1 711(3)	4 418(7)
Cl(3)	2 109(7)	1 203(3)	3 044(9)
N(1)	0 394(17)	2 141(7)	1 877(16)
N(2)	−1 374(19)	1 964(7)	1 717(17)
O(3)	−1 507(12)	0 965(6)	2 584(14)
N(4)	0 201(20)	0 490(8)	3 145(15)
C(1)	−0 663(22)	2 349(8)	1 660(19)
C(2)	−1 037(28)	2 989(8)	1 319(30)
C(3)	−0 939(23)	0 474(11)	3 022(25)
N(5)	−1 499(24)	0 080(10)	3 371(25)
C(11)	1 466(23)	2 411(11)	1 822(21)
C(12)	1 233(30)	2 709(12)	0 679(25)
C(13)	2 389(30)	2 923(13)	0 664(26)
C(14)	3 115(30)	3 278(12)	1 748(35)
C(15)	3 300(27)	3 004(15)	2 925(33)
C(16)	2 123(29)	2 827(13)	2 924(26)
C(21)	−2 699(20)	2 055(8)	1 452(17)
C(22)	−3 459(27)	1 580(11)	0 561(23)
C(23)	−4 805(24)	1 703(13)	0 243(29)
C(24)	−5 020(25)	1 706(11)	1 392(28)
C(25)	−4 272(27)	2 188(12)	2 175(29)
C(26)	−2 925(26)	2 090(12)	2 559(26)
C(31)	−2 740(20)	0 178(10)	3 253(24)
C(32)	−2 728(34)	0 418(12)	4 400(30)
C(33)	−4 085(38)	0 507(22)	4 255(36)
C(34)	−4 714(40)	−0 033(17)	4 013(50)
C(35)	−4 765(36)	−0 283(14)	2 917(30)
C(36)	−3 415(33)	−0 390(13)	2 969(36)
C(41)	1 014(23)	0 009(9)	3 376(22)
C(42)	1 524(26)	−0 151(11)	4 719(27)
C(43)	2 434(27)	−0 657(14)	4 921(29)
C(44)	1 874(29)	−1 171(11)	4 076(41)
C(45)	1 405(31)	−0 971(15)	2 862(46)
C(46)	0 505(30)	−0 489(11)	2 545(36)
H(11)	2 037	2 041	1 939
H(21)	−2 938	2 463	1 001
H(31)	−3 211	0 482	2 539
H(41)	1 719	0 201	3 191

[a] Position fixed.

TABLE 4

Anisotropic thermal parameters ($\times 10^3$) for (II), with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	53.2(4)	29.8(3)	53.7(4)	02.1(9)	23.2(3)	02.6(9)
Cl(1)	86(5)	68(4)	69(4)	−3(4)	36(4)	−20(4)
Cl(2)	100(6)	73(4)	66(5)	1(4)	31(4)	−9(4)
Cl(3)	66(4)	51(4)	129(7)	−11(3)	39(4)	6(4)
N(1)	55(11)	45(9)	47(11)	15(9)	32(9)	−1(8)
N(2)	78(15)	27(8)	49(11)	−10(11)	23(8)	8(8)
O(3)	43(8)	50(8)	82(11)	1(7)	38(8)	−8(8)
N(4)	78(15)	60(11)	14(8)	2(11)	−9(9)	5(8)
C(1)	66(15)	29(10)	41(12)	1(10)	12(11)	15(8)
C(2)	92(20)	18(10)	112(20)	12(11)	39(18)	15(13)
C(3)	44(14)	58(15)	81(19)	17(12)	9(13)	10(13)
N(5)	84(17)	58(13)	105(20)	−6(12)	35(15)	21(13)
C(11)	67(15)	63(15)	52(14)	7(12)	28(12)	−12(11)
C(12)	116(24)	73(17)	67(17)	−30(16)	57(18)	6(14)
C(13)	105(24)	73(18)	70(18)	−2(17)	34(18)	20(15)
C(14)	95(22)	55(15)	134(29)	−20(15)	72(22)	−22(17)
C(15)	65(18)	104(25)	107(26)	−22(17)	28(18)	−51(21)
C(16)	95(21)	89(20)	73(18)	−30(18)	51(17)	−19(16)
C(21)	64(14)	41(11)	36(11)	−3(10)	22(11)	3(9)
C(22)	92(19)	51(12)	62(15)	−5(13)	37(15)	5(11)
C(23)	51(16)	81(19)	96(22)	−3(14)	12(15)	5(17)
C(24)	71(17)	53(14)	97(21)	−12(13)	30(16)	−30(16)
C(25)	81(20)	68(17)	99(21)	9(15)	49(18)	2(16)
C(26)	78(18)	64(15)	82(19)	−6(14)	40(16)	−20(14)
C(31)	45(13)	49(12)	80(17)	−4(10)	20(12)	19(12)
C(32)	131(28)	50(15)	91(22)	6(17)	49(21)	−11(15)
C(33)	114(31)	168(43)	96(27)	28(30)	51(24)	−8(27)
C(34)	121(31)	93(24)	222(52)	13(23)	121(35)	49(30)
C(35)	98(10) *					
C(36)	104(25)	64(18)	121(27)	−20(17)	47(22)	−33(18)
C(41)	72(16)	33(10)	64(15)	6(10)	26(13)	6(10)
C(42)	77(18)	65(16)	85(19)	−3(14)	41(16)	14(15)
C(43)	71(18)	94(22)	85(20)	32(17)	24(16)	7(18)
C(44)	70(19)	39(13)	178(37)	21(12)	56(22)	27(18)
C(45)	82(23)	64(19)	186(41)	21(18)	44(26)	−27(25)
C(46)	105(26)	41(13)	135(29)	21(14)	35(26)	6(17)

* Refined isotropically, see text.

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares. The weighting schemes, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_0 and $\sin\theta/\lambda$, was $\surd w = 1$ for $F_0 < F^*$ and $\surd w = F^*/F_0$ for $F_0 > F^*$; F^* was 170 in (I) and 100 in (II). Calculations were made on a CDC computer at the University of London Computer Centre with programs listed in ref. 6 and on an ICL 1 904S computer at Reading University using local programs. Atomic scattering factors for tantalum, chlorine, nitrogen, and carbon were taken from ref. 7 as were corrections for the real and imaginary part of the anomalous dispersion of tantalum and chlorine. Scattering factors for hydrogen were taken from ref. 8. Both structures were refined with all non-hydrogen atoms anisotropic. The 44 hydrogen atoms from the cyclohexyl rings were included in the structure factor calculation, in tetrahedral positions with isotropic thermal parameters equivalent to those of the atom to which they were bonded, but not refined. In both structures these hydrogen atom positions were coincident with positive areas in the different Fourier map. Other hydrogen atoms on the methyl groups were not unambiguously identified in the map and were not included. Final R values were 0.075 (I) and 0.060 (II). Values of the opposite (rejected) enantiomorphs were 0.083 and 0.063 respectively. In both structures refinement was terminated when all shifts were $< 0.08\ \sigma$. In (II) there is some doubt as to the identification of some of the atoms (see Discussion section). Also, C(35) had non-positive-definite thermal parameters and was therefore refined with isotropic parameters. Adjacent atoms in this cyclohexyl ring also had highly anisotropic thermal parameters. The anisotropic thermal parameters are defined as $\exp(-2\pi^2\sum_i\sum_j U_{ij}h_ih_jb_ib_j)$ $(i,j = 1,2,3)$, b_i being the i^{th} reciprocal cell dimension. The isotropic thermal parameter is defined as $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. The zero weighted reflections in both structures show no serious discrepancies. Final difference-Fourier maps showed no significant peaks except for a region of electron density around the $00z$ and $\frac{1}{2}\frac{1}{2}z$ axes in (I) (see Discussion section). Final positional co-ordinates and thermal parameters for (I) are given in Tables 1 and 2 and for (II) in Tables 3 and 4. Molecular dimensions for both structures are compared in Table 5 except for the dimensions of the cyclohexane rings which are included in the Supplementary Publication. Carbon atoms in these rings are numbered (n1) to (n6), where n is 1—4, and specifies the ring. Hydrogen atoms are numbered such that the first two digits are

---

[7] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3178.

the same as those of the carbon atom to which they are bonded. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21 522 (14 pp., 1 microfiche).*

TABLE 5

Molecular dimensions, bond lengths (Å) and angles (°) in (I) and (II) *

	(I)	(II)
Ta–Cl(1)	2.372(9)	2.393(8)
Ta–Cl(2)	2.371(9)	2.348(8)
Ta–Cl(3)	2.435(9)	2.391(8)
Ta–N(1)	2.168(19)	2.148(19)
Ta–N(2)	2.159(19)	2.112(18)
Ta–N(3),O(3)	2.089(22)	2.087(20)
Ta–N(4)	2.158(23)	2.136(20)
Cl(1)–Ta–Cl(2)	174.7(3)	176.4(3)
Cl(1)–Ta–Cl(3)	87.7(3)	93.2(3)
Cl(2)–Ta–Cl(3)	87.1(3)	90.4(3)
Cl(1)–Ta–N(1)	96.4(7)	87.6(5)
Cl(1)–Ta–N(2)	86.4(7)	86.7(6)
Cl(1)–Ta–N(3),O(3)	101.2(7)	90.7(5)
Cl(1)–Ta–N(4)	81.9(7)	89.0(5)
Cl(2)–Ta–N(1)	83.6(7)	93.0(5)
Cl(2)–Ta–N(2)	98.1(7)	90.5(6)
Cl(2)–Ta–N(3),O(3)	82.0(7)	86.5(5)
Cl(2)–Ta–N(4)	96.1(7)	91.6(5)
N(1)–Ta–N(2)	61.7(8)	59.8(8)
N(1)–Ta–N(3),O(3)	140.0(8)	136.6(7)
N(1)–Ta–N(4)	157.5(8)	160.3(9)
N(2)–Ta–N(3),O(3)	83.7(8)	76.8(7)
N(2)–Ta–N(4)	140.0(8)	139.3(7)
N(3),O(3)–Ta–N(4)	61.6(9)	62.7(8)
Cl(3)–Ta–N(1)	79.1(6)	81.0(6)
Cl(3)–Ta–N(2)	139.3(7)	140.8(6)
Cl(3)–Ta–N(3),O(3)	136.9(6)	142.3(4)
Cl(3)–Ta–N(4)	78.5(7)	79.8(7)
N(1)–C(1)	1.34(4)	1.30(3)
N(2)–C(1)	1.40(4)	1.28(3)
N(3),O(3)–C(3)	1.33(4)	1.33(3)
N(4)–C(3)	1.33(4)	1.34(4)
C(1)–C(2)	1.51(5)	1.57(3)
C(3)–C(4),N(5)	1.56(5)	1.32(4)
N(5)–C(31)		1.48(4)
C(3)–N(5)–C(31)		120.5(22)
N(5)–C(31)–C(32)		111.4(23)
N(5)–C(31)–C(36)		108.7(24)
Ta–N(1)–C(1)	95.7(19)	92.6(15)
Ta–N(2)–C(1)	94.2(15)	94.8(15)
Ta–N(3),O(3)–C(3)	96.1(18)	94.3(16)
Ta–N(4)–C(3)	93.0(18)	92.0(16)
Ta–N(1)–C(11)	139.1(16)	136.5(15)
Ta–N(2)–C(21)	132.2(16)	139.3(15)
Ta–N(3)–C(31)	135.6(19)	
Ta–N(4)–C(41)	140.8(22)	140.1(21)
C(11)–N(1)–C(1)	124.5(23)	130.5(19)
C(21)–N(2)–C(1)	127.2(23)	125.0(18)
C(31)–N(3)–C(3)	126.4(26)	
C(41)–N(4)–C(3)	125.9(26)	126.4(23)
N(1)–C(1)–N(2)	108.3(24)	111.2(18)
N(1)–C(1)–C(2)	127.3(30)	124.5(24)
N(2)–C(1)–C(2)	124.2(27)	124.3(24)
N(3),O(3)–C(3)–C(4),N(5)	124.1(29)	118.9(27)
N(3),O(3)–C(3)–N(4)	109.2(27)	110.9(25)
N(4)–C(3)–C(4),N(5)	126.5(28)	129.8(24)

* Dimensions of the cyclohexyl rings are given in Supplementary Publication.

DISCUSSION

The molecules (I) and (II) are shown in Figures 1 and 2 respectively with the atomic numbering scheme used. In both structures the tantalum atom is seven-coordinate with a distorted pentagonal bipyramidal geometry; the two chloride atoms are in axial positions, while the third chlorine atom is equatorial, together with the two bidentate ligands. (I) $\{[TaCl_3L^1_2]$, $L^1 = C_6H_{11}NC(Me)NC_6H_{11}\}$ is similar in stoicheiometry and geometry to the others in the series.[1-4] However in (II) $\{[TaCl_3L^1L^2]$; see Figure 2$\}$, while one of the bidentate ligands is L^1, the other is L^2 in which one of the cyclohexyl groups has shifted away from the tantalum atom thus considerably relieving crowding in the girdle. (II) was obtained from our first attempt to prepare crystals of (I) and we concluded that some rearrangement of the ligand had occurred to minimise the steric repulsions between cyclohexane rings. However as subsequent preparations have always led to (I), in which the four cyclohexyl rings are in the pentagonal girdle, and as steric effects are not excessive, it seems more likely that the preparation of (II) was due to some impurity of the ligand.

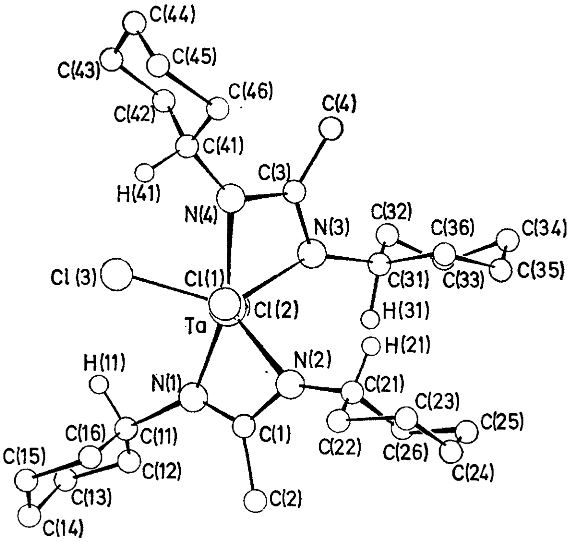


FIGURE 1 The molecule of (I)

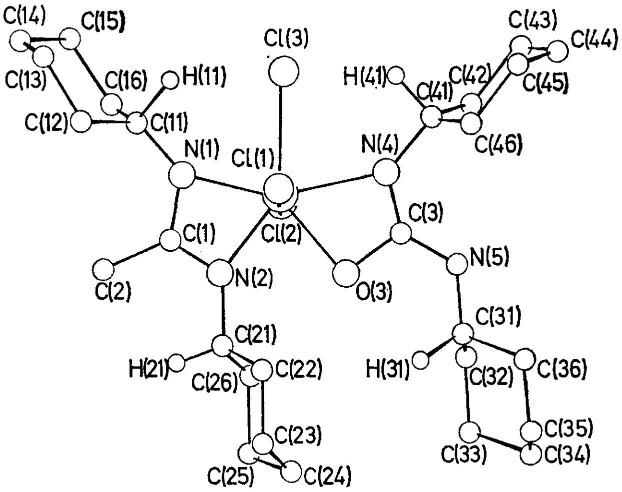


FIGURE 2 The molecule of (II)

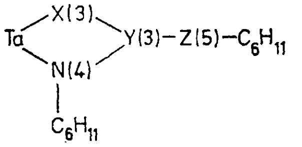
However, the structure determination of (II) was not

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

sufficiently accurate for us to be able to distinguish between all possible atomic arrangements in L^2. Nevertheless, taking into account the results of several least-squares refinements, together with the molecular dimensions and the necessity of finding a reasonable route from L^1 to L^2 for the preparation of (II), we conclude (see later) that L^2 is $C_6H_{11}NC(NHC_6H_{11})O$.

First we attempted to identify the atoms in L^2 as carbon, nitrogen, or oxygen. We assumed that N(4) was a nitrogen atom, and that the two cyclohexane rings were unaltered, but made no other assumptions. This leaves three atoms [X(3), Y(3), and Z(5); see diagram] which we refined in turn with carbon, nitrogen, and oxygen scattering factors. For X(3) isotropic thermal parameters were 0.018, 0.040, and 0.052 Å^2, for Y(3) 0.064, 0.081, and 0.105 Å^2, and for Z(5) 0.062, 0.078, and 0.100 Å^2. These results are not conclusive, but by comparisons with the thermal parameters of atoms in close proximity,* it seems probable that X is N or O, Y is C or N, and Z is C or N. Chemically it seemed probable that the R–N–C–N–R linkage would be maintained and this would support a Y=C, Z=N assignment. This is supported by the molecular dimensions. The Y(3)–Z(5) bond length is 1.32(4) Å and thus contains a considerable amount of double-bond character. The X(3)–Y(3)–Z(5)–C(31) torsion angle is 1.4°, suggesting that Z(5) is bonded to one hydrogen atom, since with two in tetrahedral positions, a much larger angle would be expected. It therefore seems unlikely that Z is a carbon atom as with a –CH group the molecule would either contain Ta^{VI} or be an anion, both impossibilities.



L^2 is therefore R–N–C(NHR)NH or R–N–C(NHR)O. Both possibilities were refined and gave R values of 0.0605 (for –NH) and 0.0603 (for O). Both formulations of the ligand could easily be obtained by reaction of water or ammonia on RN:C:NR [9] and would also react with $MeTaCl_3L$ to give $TaCl_3L^1L^2$.[10] In our method of preparation, water is the more likely impurity. A difference-Fourier map did not unambiguously show a hydrogen atom bonded to X(3). A hydrogen atom placed in a trigonal position would be 1.58 from one on C(22) and 1.69 Å from one on C(26). While these values could, by some distortion of angle, be increased to an acceptable 2.0 Å, this seems unlikely.† All this evidence suggests that L^2 is R–N–C(NHR)–O and the final refinement assumes this assignment.

The geometries of (I) and (II) can be compared and with those found for other molecules in the series, notably $TaCl_3(Pr^iN\text{–}C(Me)\text{–}NPr^i)_2$ (III) [1,2]. The difference in stoicheiometry between (I) and (III) is confined to the replacement of four cyclohexyl by four isopropyl groups. The geometry of (I) is similar to that found in the monoclinic [1] rather than in the orthorhombic form [2] of (III) in that the distortion from the ideal P.B. has C_2 symmetry with the two-fold axis approximately co-axial with the Ta–Cl(3) bond. The Ta–Cl bond lengths are equivalent to those found in (III), the equatorial bond being *ca.* 0.06 Å longer than the axial bonds. The two four-membered rings are planar but twisted by 12.4 and 15.5° out of the plane of the girdle (see Table 6) in opposite directions such that N(2) and N(3) are –0.29 and 0.34 Å from it. These twists significantly increase the contact distances between isopropyl groups on N(2) and N(3). The planes of the two four-membered rings intersect at 27.3°. The Cl(3) · · · R(n) (n = 1 or 4, R = cyclohexyl) contacts are increased by this twist in the rings and also by the large Ta–N(n)–C(n1) angles [139.1(16) and 140.8(22)°] and by the fact that the C(n1) atoms are –0.17 and –0.07 Å out of the planes of the respective four-membered rings. The cyclohexyl rings are orientated such that the Ta–N(n1)–C(n1)–H(n1) torsion angles (see Table 7) are *ca.* 0° with atoms H(11) and H(41) in close proximity with Cl(3). The C(m1) * (m = 2 or 3) atoms are 0.50 and 0.32 Å from the four-membered rings, a greater distance than that found for the C(n1) atoms, no doubt owing to the greater crowding in these positions. The orientations of the cyclohexyl

TABLE 6

Least-squares planes for (I) and (II). Equations are in the form $Ax + By + Cz = D$, where x,y,z are the crystallographic co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets

Plane (1): Ta, Cl(3), N(1), N(2), N(3) [or O(3)], N(4)

	A	B	C	D
(I):	17.76	2.27	–7.60	3.07
(II):	–2.02	8.99	11.00	3.95

[(I) Ta –0.02, Cl(3) 0.03, N(1) 0.18, N(2) –0.29, N(3) 0.34, N(4) –0.23, C(1) –0.08, C(2) –0.25, C(3) 0.05, C(4) 0.13, C(11) 0.64, C(21) –1.08, C(31) 1.05, C(41) –0.64; (II) Ta 0.01, Cl(3) 0.06, N(1) –0.04, N(2) –0.01, O(3) 0.07, N(4) –0.09, C(1) 0.12, C(2) 0.40, C(3) –0.01, N(5) 0.14, C(11) –0.07, C(21) 0.05, C(31) 0.34, C(41) –0.43]

Plane(2): Ta, N(1), N(2)

	A	B	C	D
(I):	14.34	–1.35	–8.68	1.42
(II):	–1.93	9.49	10.87	4.00

[(I) C(1) 0.02, C(2) 0.15, C(11) –0.17, C(21) 0.50; (II) C(1) 0.17, C(2) 0.48, C(11) –0.01, C(21) 0.06]

Plane (3): Ta, N(3) [or O(3)], N(4)

	A	B	C	D
(I):	19.14	8.42	–6.30	4.43
(II):	–1.39	7.96	11.00	3.82

[(I) C(3) –0.04, C(5) –0.05, C(31) 0.32, C(41) –0.07; (II) C(3) 0.01, N(5) 0.16, C(31) 0.28, C(41) –0.24]

Angles (°) between planes: (I), (1)–(2) 12.4, (1)–(3) 15.5, (2)–(3) 27.3; (II) (1)–(2) 1.3, (1)–(3) 4.1, (2)–(3) 4.9.

---

* N(1), 0.043, N(2) 0.049, N(4) 0.056, C(1) 0.048, C(2) 0.075, C(31) 0.058, C(41) 0.055 Å^2. Standard deviations of these parameters and of those quoted in the text are *ca.* 0.005 Å^2. Isotropic thermal parameters were used in order to facilitate comparisons. In the final refinement, anisotropic parameters were used.

† It is certainly impossible for X(3) to have two hydrogen atoms bonded in tetrahedral positions as one of these would be just 1.25 Å from a hydrogen atoms on C(22).

[9] F. Kurzer and K. Dourachi-Zadeh, *Chem. Rev.*, 1967, **67**, 107.

[10] M. G. B. Drew and J. D. Wilkins, *J. Organometallic Chem.*, 1974, **69**, 111.

groups R(*m*) around N(*m*) are similar in that the Ta–N(*m*)–C(*m*1)–H(*m*1) torsion angles are also *ca.* 0°; thus the H(*m*1) atoms are in the most sterically crowded positions; H(21) · · · H(31) is 2.42 Å. In (I) there are no abnormally close contacts between adjacent cyclohexyl groups. While the majority of Ta–N bonds are similar to those in (III), Ta–N(4) is slightly longer than expected. Thus the structures of (I) and (III) are remarkably similar, there being no major difference between the two geometries. We calculated the best molecular fit on the 28 comparable atoms in (I) and (III), *i.e.* all atoms in Table 1 except for C(*n*3), C(*n*4), C(*n*5) with *n* = 1—4, using our programs based on the methods of Dollase[11] and Nyburg.[12] The mean root-mean-square separation of equivalent atoms was 0.11 Å, the maximum separation being 0.24 Å. This agreement contrasts with analogous $MeTaCl_2$ complexes[3,4] where replacement of isopropyl by cyclohexyl groups totally changes the geometry. The probable reason for the similar geometries in (I) and (III) is that the requirement for the three chlorine atoms to be in the T formation is paramount.

TABLE 7

Torsion angles (°) for (I) and (II) *

	(I)	(II)
Cl(3)–Ta–N(4)–C(41)	−21.2	−19.8
Cl(3)–Ta–N(1)–C(11)	−21.1	1.7
Ta–N(1)–C(11)–H(11)	−1.6	17.9
Ta–N(1)–C(11)–C(12)	110.5	136.9
Ta–N(1)–C(11)–C(16)	−108.7	−96.8
Ta–N(4)–C(41)–H(41)	−7.0	5.3
Ta–N(4)–C(41)–C(42)	107.8	120.2
Ta–N(4)–C(41)–C(46)	−120.1	−110.6
Ta–N(2)–C(21)–H(21)	22.1	−179.0
Ta–N(2)–C(21)–C(22)	−95.5	−62.8
Ta–N(2)–C(21)–C(26)	138.7	63.6
C(3)–N(5)–C(31)–H(31)		25.4
C(3)–N(5)–C(31)–C(32)		−94.2
C(3)–N(5)–C(31)–C(36)		145.7
Ta–N(3)–C(31)–H(31)	13.9	
Ta–N(3)–C(31)–C(32)	−99.2	
Ta–N(3)–C(31)–C(36)	128.7	
N(3),O(3)–Ta–N(2)–C(21)	−48.0	2.6
N(2)–Ta–N(3)–C(31)	−38.3	
N(3)–C(3)–N(5)–C(31)		1.4

* C–C–C–C torsion angles in cyclohexane rings are given in Supplementary Publication.

The major differences in geometry between (II) and (I) are a consequence of the cyclohexyl groups being bonded to N(5) and not O(3). As might be expected, the molecule is far less distorted * from an ideal P.B. than is (I) or (III). Least-squares planes (Table 6) show the mean

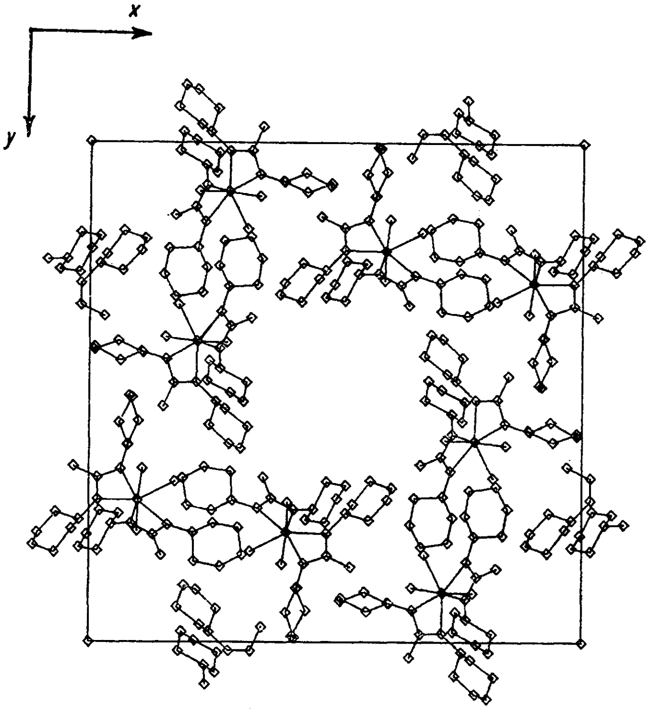


FIGURE 3 Unit cell of (I) in the *c* projection

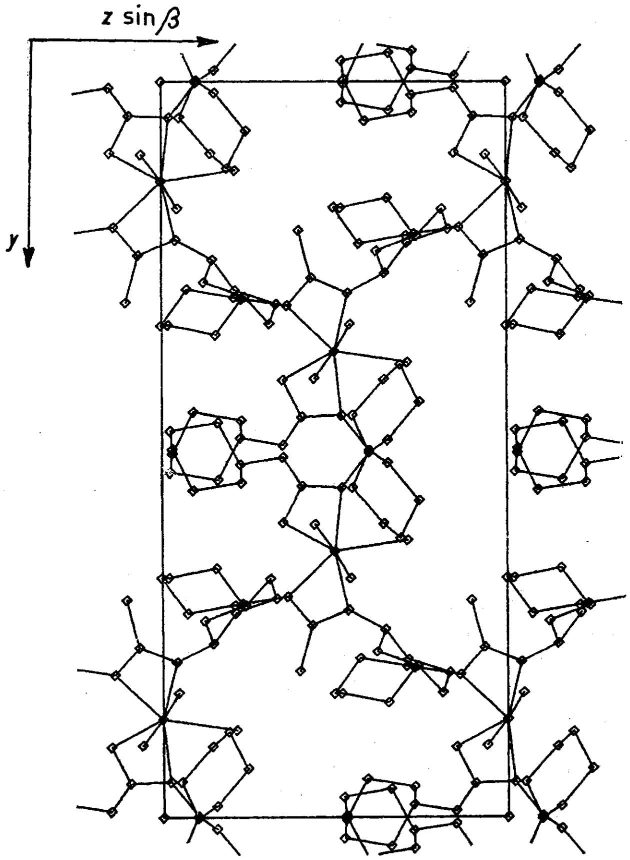


FIGURE 4 Unit cell of (II) in the *c* projection

---

* The use of distorted in this context has been described as ' an irksome phrase, encumbered with imprecise English ' (E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 1974, **96**, 1748). We agree that it is helpful to attempt to quantify distortions from ideal geometries. We have used the method of ref. 11 to obtain values of the root-mean-square mean separation of equivalent points in observed co-ordination spheres after dilation and rotation with those in a co-ordination sphere of radius 1 Å with an ideal geometry. Values of 0.231 and 0.095 Å respectively were obtained for (I) and (II) when compared to D_{5h} symmetry. A similar calculation, but using all 39 atoms, gave 0.064 Å for the root-mean-square mean separation in (I) from a C_2 geometry. This value was sufficiently low to suggest that distortions from C_2 geometry are due only to packing forces.

[11] W. A. Dollase, *Acta Cryst.*, 1974, **A30**, 513.

[12] S. C. Nyburg, *Acta Cryst.*, 1974, **B30**, 251.

deviation of a contributing atom from the $TaClN_3O$ plane is only 0.05 *vs.* 0.18 Å for the $TaClN_4$ plane in (I). The angles made by the four-membered rings with the equatorial plane are 1.3 and 4.1°, and these intersect at 4.9°. The maximum deviation from 90° of an angle subtended at tantalum by an axial chlorine and a nitrogen or oxygen atom is 3.5°.

In (II), the Ta–N(2)–C(21)–H(21) torsion angle is −179.0° and not *ca.* 0° as found elsewhere.[1-4] This rotation is concomitant with a closely planar equatorial girdle, as C(22) and C(26) are thus equal distances above and below the plane and equidistant from O(3). The N(2)–Ta–O(3) angle is 76.8(7) compared to 83.7(8)° for N(2)–Ta–N(3) in (I), a consequence of the absence of the bulky cyclohexyl groups on O(3). The orientation of this cyclohexyl group leads to a potentially close C(2)···H(21) contact (see Figure 2) but this is increased (to 2.50 Å) by C(2) being 0.48 Å from the Ta, N(1), N(2) plane.

The Cl(3)–Ta–N(4)–C(41) torsion angle is −19.8° [−21.2° in (I)] while Cl(3)–Ta-N(1)–C(11) is 1.7° [(I) −21.1°]. This discrepancy is also a consequence of the orientation of R(2) in that the Ta, N(1), N(2), C(1) ring is closer to the equatorial plane than is the Ta, O(3), N(4), C(3) ring. O(3) has four contacts to the hydrogen atoms on C(22) and C(26) in the range 2.67—2.77 Å. A similar effect is noted[2] in the orthorhombic form of (III) in that when a Ta–N–C–H torsion angle is 180° rather than 0°, then the four-membered ring is coplanar with the girdle. The orientation of ring 3 is shown in Figure 2; the C(3)–N(5)–C(31)–H(31) torsion angle is 26.9°. There are no exceptionally close intramolecular contacts between cyclohexyl rings.

The Ta–Cl bond lengths are within the usual range. The axial Ta–Cl(3) bond is shorter than found in (I) and (III), presumably because of less steric crowding. One of the axial bonds is longer than the other but we can see no reason for this. The Ta–N bonds are also short (mean 2.134 Å). The Ta–O bond length is 2.087(20) Å.

In both structures, packing is *via* the usual van der Waals forces. The two unit cells, both in the *c* projection, are shown in Figures 3 and 4. There are very few contacts < 3.75 Å between molecules, only six in (I) and four in (II), and these are listed in the Supplementary Publication. As can be seen from Figure 3, there are large cylindrical holes around the 00*z* and $\frac{1}{2}\frac{1}{2}z$ axes in (I). Indeed the non-hydrogen atom closest to this axis lies 4.8 Å from it. This accounts for the exceptionally low value of D_c (1.35 g cm^{-3}) for (I) compared with those for related compounds (*ca.* 1.51). A difference-Fourier map showed some residual electron density in these holes but there were no distinct peaks, the maximum being *ca.* 0.25 of a carbon atom. Attempts to refine broad regions of electron density were not successful although *R* was reduced to 0.073. We conclude that some disordered solvent molecules occupy these channels but we were not able to identify them.

We thank A. W. Johans for his assistance with the crystallographic investigations.

[5/881 *Received*, 9*th May*, 1975]