X-Ray Crystal Structures of Ti(IV)-4,4′-Methylenebis(antipyrine) Complexes, $[Ti(dam)_3](ClO_4)_4$. Formation of Eight-Membered Chelate Rings and Aromatic Ring Stacking Responsible for Characteristic Coloration

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X-Ray crystallographic studies have been made for two Ti(IV) complexes with 4,4′-methylenebis(antipyrine) (so-called diantipyrylmethane, abbreviated to dam) used for spectrophotometry of Ti(IV). The crystal data and final R values are: $[Ti(dam)_3](ClO_4)_4$ (**1**), triclinic, $P\bar{1}$, a=15.099(2), b=22.308(2), c=14.015(2) Å, α=100.00(1), β=116.68(1), γ=87.16(1)°, V=4151(1) Å^3, Z=2, R=0.124 for 8060 reflections; $[Ti(dam)_3](ClO_4)_4 \cdot H_2O$ (**2**), monoclinic, $P2_1/c$, a=14.075(3), b=29.127(7), c=21.386(6) Å, β=122.42(1)°, V=7401(3) Å^3, Z=4, R=0.105 for 6685 reflections. The reagent dam acts as a bidentate ligand to form eight-membered chelate rings. Between a pyrazolone moiety of one ligand and a phenyl ring of another prevails aromatic ring stacking, which gives extra stability to these complexes and is responsible for the characteristic charge transfer band around 385 nm.

4,4′-Methylenebis(antipyrine) (so-called as diantipyrylmethane abbreviated to dam; Fig. 1) reacts with titanium(IV) in a strongly acidic medium to form a yellow complex having an absorption maximum at around 385 nm. This reaction has widely been used for selective photometric determination of titanium(IV).[1–10]

Although the metal-to-ligand ratio of the species was determined to be 1:3, the exact composition including the hydrolysis degree of Ti(IV) center has been unknown. Provided dam forms a chelate ring (Fig. 1), it will be a large one containing not less than eight members, which is known to be hardly formed.[11,12] Furthermore, the mechanism for strong coloration upon coordination to titanium(IV) is not clear.

Preparative works in a strongly acidic medium used for spectrophotometry afforded two kinds of crystalline compounds having the composition of $[Ti(dam)_3](ClO_4)_4$. To elucidate the points mentioned above, we have made X-ray crystal structure analysis for these compounds and found unusual eight-membered chelate rings and remarkable aromatic ring stacking responsible for the coloration.

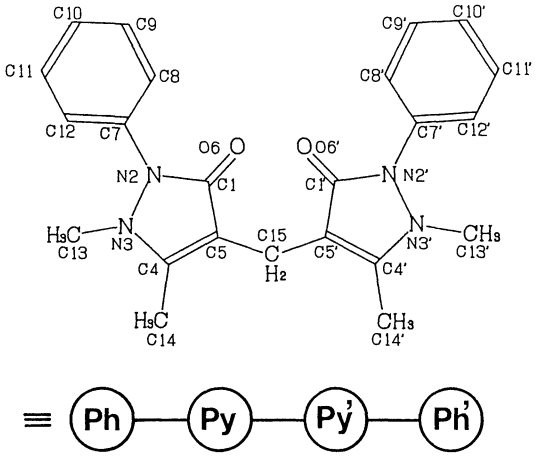

Fig. 1 Atom-numbering system of diantipyrylmethane.

Experimental

Preparation of the Complexes. Titanium(IV) tetrachloride was reacted with 4,4′-Methylenebis(antipyrine) in perchloric acid solution. Slow evaporation gave only small amounts of orange crystals(**1**) together with yellow powder. We could not perform chemical analysis for the complex **1**.

After these were filtered off, the filtrate was further stood to give larger amounts of violet crystals(**2**). Found: C, 50.53; H, 4.57; N, 10.41%. Calcd for $[Ti(dam)_3](ClO_4)_4 \cdot H_2O$: C, 50.86; H, 4.59; N, 10.32%. The water content determined by Karl Fischer's method (1.1%) was in good agreement with the calculated value (1.11%). The compound **2**, when ground, changes in color to orange similar to crystalline **1**.

X-Ray Analysis. Crystallographic details for **1** and **2** are given in Table 1. The space group of **1** was possible to be either $P1$ or $P\bar{1}$, but was determined to be the latter, after the structure refinement, on the basis of the significance test of the R values for the respective space groups. Intensity data were collected on a Rigaku AFC-5R diffractometer with graphite-monochromatized Cu $K\alpha$ radiation (λ=1.54178 Å). The ω–2θ scan technique was employed with an ω-scan width of (1.2+0.2 tan θ) deg at a scan rate of 6 deg min^{-1} with 5 s background counts. No significant variations in intensities of 3 standard reflections monitored every 100 measurements were observed during data collection.

The structures were solved by the conventional heavy-atom method. In difference Fourier maps for **1** and **2** synthesized without the contributions of the perchlorate O atoms, five or more peaks were found around respective Cl atoms. We assumed the O atoms to be disordered, but could not clearly interpret the arrangement of peaks on the basis of any superpositions of the disordered anions. For each anion, four rather high peaks exhibiting an approximate configuration of the anion were adopted and kept fixed during refinement. The geometries thus obtained are of less accuracy: mean Cl–O=1.43 Å (ranging in 1.29—1.66 Å),

Table 1. Crystallographic Details for **1** and **2**

	1	**2**
Formula	$C_{69}H_{72}N_{12}O_{22}Cl_4Ti$	$C_{69}H_{74}N_{12}O_{23}Cl_4Ti$
Formula weight	1611.1	1629.1
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	15.099(2)	14.075(3)
b/Å	22.308(2)	29.127(7)
c/Å	14.015(2)	21.386(6)
α/deg	100.00(1)	—
β/deg	116.68(1)	122.42(1)
γ/deg	87.16(1)	—
V/Å^3	4151(1)	7401(3)
Z	2	4
ρ_{calcd}/g cm^{-3}	1.289	1.462
μ(Cu $K\alpha$)/cm^{-1}	27.3	30.8
Crystal size/mm	0.3×0.2×0.1	0.3×0.1×0.1
$2\theta_{max}$/deg	110	120
No. of unique reflections	10417	10993
No. of observed reflections with $F_o>3\sigma(F_o)$	8363	6874
R	0.124	0.105
R_w	0.180	0.148
S (goodness of fit)	1.145	1.253
No. of reflections used at the last stage of refinement	8060	6685

1.37 Å (1.18—1.46 Å); mean O-Cl-O=108° (83—137°), 109° (99—122°) for **1** and **2**, respectively. Though the results of Karl Fischer's method suggested the crystal of **2** to be monohydrated, we could not locate any water molecule in a difference Fourier map.

The structures were refined by the block-diagonal least-squares technique using the positional and anisotropic thermal parameters for the non-H atoms excluding disordered perchlorate O atoms for which only isotropic temperature factors were refined. No H atoms were located. Absorption corrections were applied after isotropic least-squares refinement by an empirical method based on the differences between the observed and calculated structure factors.[13] Atomic scattering factors were evaluated by analytical procedures, $f=\sum[a_i \exp(-b_i \lambda^{-2} \sin^2\theta)]+c$ (i=1, ··, 4).[14] Weights were taken as $w=[\sigma^2(F_o)+c^2|F_o|^2]^{-1}$ for the reflections with $w^{1/2}|\Delta F|<4$, and w=0 otherwise. The values of c^2 were 0.02297 and 0.00966 for **1** and **2**, respectively. No peaks larger than 0.5 e Å^{-3} were found in the last difference electron density maps of **1** and **2**. Comparatively large R values for **1** and **2** may be due to the poor quality of intensity data measured by using very small and inferior crystals and to the disordered structures of ClO_4 anions. Computations using the programs of PLUTO and XPACK86 SHIONOGI were performed on a FACOM M-730 computer at Shionogi Research Laboratories.[15]

Results and Discussion

Atomic coordinates and equivalent isotropic temperature factors for **1** and **2** are listed in Table 2. Stereoscopic views of the cations are represented in Fig. 2. The atoms of one ligand referred to as (A) in the respective complex ions are numbered as shown in Fig. 1, and those of the other two ligands (B and C) are represented by the corresponding numbers of 100 and 200 levels. The ClO_4 anions are given by the numbers

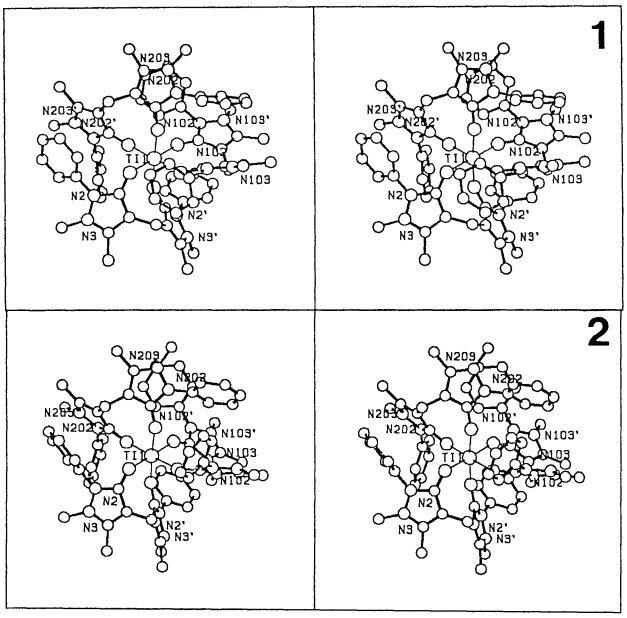

Fig. 2 Stereoscopic views of **1** and **2**.

of 300 level. The four anions of **1** are statistically distributed at five locations: two of them labeled as Cl(300) and Cl(310) are fully occupied and the other three labeled as Cl(320), Cl(330), and Cl(340) with partial occupancy of 2/3.

Coordination Geometry around Ti(IV). The metal-ligand distances and angles for **1** and **2** are summarized in Table 3. The Ti–O distances (av 1.93 Å for **1** and 1.94 for **2**) are shorter than those of other Ti(IV) complexes hexa-coordinated only by oxygen atoms, such as $Ti_2O_2(acac)_4$ (2.01 Å; acac=acetylacetonate),[16] $Ti(OR)_2(acac)_2$ (1.96 Å; OR=2,6-diisopropyl-

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors (Å$^2\times 10$) with esd Values in Parentheses for **1** and **2**

Atom	**1**				**2**			
	x	y	z	B_{eq}/B[a)]	x	y	z	B_{eq}/B[a)]
Ti	2621.8(7)	2689.6(5)	7969.5(8)	29.2(4)	4742(1)	975.3(5)	7102.3(8)	26.1(5)
C(1)	3821(4)	3516(3)	10059(5)	31(2)	3277(7)	1133(3)	5436(5)	34(3)
N(2)	3620(4)	3822(3)	10867(4)	39(2)	2724(6)	870(3)	4827(4)	38(3)
N(3)	4470(4)	3858(3)	11824(4)	44(2)	1982(6)	1150(3)	4244(4)	44(3)
C(4)	5193(5)	3602(3)	11608(5)	41(2)	2081(7)	1577(4)	4513(5)	41(4)
C(5)	4818(5)	3383(3)	10512(5)	36(2)	2860(7)	1579(3)	5249(5)	36(3)
O(6)	3123(3)	3408(2)	9065(3)	33(1)	4072(4)	951(2)	6066(3)	33(2)
C(7)	2661(5)	4002(3)	10786(6)	37(2)	2857(8)	396(3)	4730(5)	40(4)
C(8)	2313(6)	3787(4)	11414(7)	51(3)	2384(10)	62(4)	4953(6)	63(5)
C(9)	1408(7)	3982(5)	11365(8)	66(4)	2548(11)	−397(5)	4877(7)	79(6)
C(10)	859(8)	4364(5)	10621(10)	77(5)	3151(12)	−522(5)	4567(7)	73(6)
C(11)	1197(8)	4551(5)	9961(9)	74(4)	3597(14)	−206(4)	4338(10)	85(9)
C(12)	2145(6)	4387(3)	10073(7)	51(3)	3460(12)	262(4)	4432(8)	69(7)
C(13)	4563(7)	4265(4)	12825(6)	62(3)	1206(11)	942(6)	3507(6)	83(6)
C(14)	6238(6)	3576(4)	12498(7)	60(3)	1402(9)	1965(4)	4029(7)	60(5)
C(15)	5388(5)	3056(3)	9926(6)	42(3)	3282(8)	1985(3)	5765(5)	40(4)
C(1′)	4423(5)	2036(3)	9345(5)	36(2)	2938(6)	1697(3)	6773(5)	32(3)
N(2′)	4643(4)	1434(3)	9306(5)	40(2)	2356(6)	1840(2)	7084(4)	37(3)
N(3′)	5638(4)	1395(3)	9677(5)	47(2)	1879(7)	2264(3)	6767(5)	44(3)
C(4′)	6053(5)	1964(4)	10001(6)	41(3)	2086(8)	2348(3)	6236(6)	45(4)
C(5′)	5296(5)	2380(3)	9775(5)	38(2)	2776(7)	2015(3)	6227(5)	39(4)
O(6′)	3508(3)	2206(2)	9005(4)	37(2)	3510(5)	1325(2)	7002(3)	35(2)
C(7′)	3948(5)	938(3)	8721(6)	41(3)	2544(8)	1697(3)	7786(6)	43(4)
C(8′)	3213(7)	869(4)	8998(8)	54(4)	2815(8)	2034(3)	8314(6)	46(4)
C(9′)	2506(8)	382(4)	8436(10)	69(5)	3035(9)	1896(4)	9011(6)	54(5)
C(10′)	2593(8)	−22(4)	7589(8)	66(4)	2979(10)	1425(4)	9139(7)	59(5)
C(11′)	3326(8)	47(4)	7334(8)	65(4)	2708(10)	1108(4)	8600(7)	56(5)
C(12′)	4033(7)	538(3)	7904(7)	55(3)	2483(9)	1250(3)	7902(6)	47(5)
C(13′)	6141(7)	830(4)	10062(8)	69(4)	882(11)	2420(5)	6783(8)	73(6)
C(14′)	7154(6)	2081(5)	10506(8)	63(3)	1585(11)	2765(4)	5752(8)	67(6)
C(101)	3848(5)	2746(3)	6741(5)	35(2)	6222(7)	1831(3)	7620(5)	32(3)
N(102)	4151(5)	3245(3)	6524(5)	46(2)	7098(6)	1984(2)	7572(5)	40(3)
N(103)	4417(5)	3054(3)	5701(5)	52(3)	7726(7)	2287(3)	8147(5)	49(4)
C(104)	4228(6)	2452(4)	5388(7)	53(3)	7218(8)	2328(3)	8543(6)	44(4)
C(105)	3883(5)	2239(3)	6036(5)	39(2)	6279(7)	2055(3)	8219(5)	36(4)
O(106)	3664(3)	2790(2)	7565(3)	38(2)	5528(4)	1535(2)	7147(3)	33(2)
C(107)	4516(7)	3816(4)	7269(7)	54(3)	7436(8)	1853(3)	7078(6)	42(4)
C(108)	5497(8)	3915(5)	7877(8)	71(4)	6738(10)	1924(4)	6327(6)	54(5)
C(109)	5881(10)	4413(5)	8687(11)	89(6)	7125(12)	1784(4)	5867(7)	65(6)
C(110)	5141(12)	4833(6)	8794(10)	98(6)	8169(12)	1627(4)	6157(9)	70(7)
C(111)	4211(13)	4734(6)	8246(13)	101(8)	8871(12)	1542(4)	6913(10)	79(8)
C(112)	3796(8)	4193(4)	7386(9)	70(5)	8515(10)	1654(4)	7398(8)	62(6)
C(113)	4743(9)	3484(6)	5253(10)	83(5)	8464(12)	2619(5)	8102(9)	79(8)
C(114)	4409(8)	2106(6)	4491(8)	74(5)	7677(10)	2628(4)	9205(7)	62(5)
C(115)	3761(5)	1594(3)	6127(6)	43(3)	5427(7)	2029(3)	8432(5)	35(4)
C(101′)	2074(5)	1524(3)	6145(5)	34(2)	5551(7)	1169(3)	8748(5)	37(3)
N(102′)	1236(4)	1153(3)	5603(4)	39(2)	5729(6)	905(2)	9330(4)	36(3)
N(103′)	1332(5)	772(3)	4770(5)	45(2)	5948(6)	1203(3)	9893(4)	37(3)
C(104′)	2252(5)	863(3)	4876(6)	44(3)	5841(7)	1637(3)	9652(5)	36(3)
C(105′)	2717(5)	1347(3)	5703(5)	38(2)	5586(7)	1629(3)	8933(5)	33(3)
O(106′)	2112(4)	1960(2)	6890(4)	47(2)	5441(5)	978(2)	8168(3)	37(2)
C(107′)	309(5)	1253(3)	5645(6)	39(2)	6030(7)	432(3)	9430(5)	36(4)
C(108′)	280(6)	1323(4)	6613(6)	49(3)	7084(9)	301(4)	9999(6)	51(4)
C(109′)	−602(6)	1436(5)	6649(8)	62(3)	7349(11)	−175(4)	10021(8)	69(6)
C(110′)	−1469(6)	1491(4)	5703(9)	65(4)	6600(11)	−467(4)	9471(7)	62(6)
C(111′)	−1432(6)	1416(4)	4765(8)	66(4)	5543(12)	−320(4)	8906(7)	61(6)
C(112′)	−542(6)	1307(4)	4684(7)	52(3)	5245(9)	137(3)	8890(5)	43(4)
C(113′)	745(7)	189(4)	4262(8)	58(4)	5970(11)	1035(4)	10549(6)	58(5)
C(114′)	2589(8)	494(5)	4117(10)	80(5)	6067(10)	2041(4)	10157(6)	57(5)
C(201)	852(5)	3096(3)	6193(5)	41(2)	6574(6)	259(3)	7574(5)	31(3)
N(202)	530(4)	2859(3)	5120(4)	45(2)	7627(6)	236(2)	8218(4)	39(3)
N(203)	−518(4)	2859(3)	4644(5)	48(2)	7940(6)	−227(3)	8319(5)	46(3)
C(204)	−791(5)	3078(4)	5381(6)	48(3)	7072(7)	−473(3)	7788(6)	44(4)

Table 2. (Continued)

Atom	1				2			
	x	y	z	B_{eq}/B[a)]	x	y	z	B_{eq}/B[a)]
C(205)	39(5)	3247(3)	6390(6)	44(3)	6230(7)	−181(3)	7292(5)	39(4)
O(206)	1792(3)	3163(2)	6847(4)	43(2)	6104(4)	646(2)	7300(3)	34(2)
C(207)	1060(6)	2824(4)	4498(6)	45(3)	8432(7)	583(3)	8583(5)	39(3)
C(208)	1116(6)	2275(4)	3890(6)	50(3)	8326(10)	901(4)	9039(6)	55(5)
C(209)	1592(8)	2258(5)	3243(8)	65(4)	9125(11)	1231(4)	9390(7)	68(6)
C(210)	2065(8)	2759(5)	3271(8)	73(4)	10087(10)	1252(4)	9344(8)	73(6)
C(211)	2013(8)	3318(5)	3893(8)	69(4)	10178(10)	936(5)	8916(8)	73(6)
C(212)	1503(8)	3345(4)	4502(6)	61(3)	9368(8)	599(4)	8517(7)	54(5)
C(213)	−1094(6)	2674(5)	3471(7)	64(3)	8904(9)	−383(4)	9028(6)	61(5)
C(214)	−1858(7)	3130(5)	5178(9)	74(4)	7111(11)	−988(3)	7778(8)	68(6)
C(215)	67(6)	3574(4)	7422(6)	49(3)	5124(7)	−286(3)	6610(5)	39(4)
C(201′)	884(5)	2748(3)	8600(6)	36(2)	3737(6)	−17(3)	6974(5)	30(3)
N(202′)	691(4)	2485(3)	9306(5)	43(2)	2990(6)	−218(2)	7107(4)	35(3)
N(203′)	−133(5)	2724(3)	9349(6)	53(3)	2910(6)	−682(2)	6921(5)	39(3)
C(204′)	−487(6)	3137(4)	8665(8)	59(4)	3679(7)	−768(3)	6736(5)	36(3)
C(205′)	127(5)	3171(4)	8193(6)	45(3)	4210(6)	−368(3)	6772(4)	31(3)
O(206′)	1602(3)	2582(2)	8389(4)	37(2)	3970(5)	415(2)	7098(3)	33(2)
C(207′)	1252(6)	2023(3)	9915(6)	43(3)	2065(7)	−18(3)	7123(5)	37(4)
C(208′)	2258(6)	2143(4)	10598(6)	53(3)	1303(8)	265(3)	6527(6)	42(4)
C(209′)	2779(8)	1701(6)	11204(8)	82(5)	372(9)	429(4)	6521(7)	57(5)
C(210′)	2317(10)	1158(6)	11118(10)	90(6)	246(9)	322(4)	7101(8)	60(6)
C(211′)	1334(11)	1041(5)	10389(10)	92(6)	1007(10)	64(4)	7684(7)	53(5)
C(212′)	777(8)	1482(5)	9786(9)	68(5)	1944(8)	−103(3)	7704(5)	44(4)
C(213′)	−431(8)	2622(6)	10182(9)	73(5)	2180(9)	−1005(3)	6990(7)	56(5)
C(214′)	−1393(8)	3503(6)	8537(10)	79(5)	3805(10)	−1233(3)	6492(7)	54(5)
Cl(300)	9412(2)	889(1)	1499(2)	58(1)	4186(2)	1766(1)	4060(2)	50(1)
O(301)	8817	970	2092	113(2)	4247	2022	4643	71(2)
O(302)	10418	827	2197	137(4)	4291	1304	4217	80(2)
O(303)	9548	1544	1431	195(6)	4950	1935	3938	71(2)
O(304)	9106	341	766	252(9)	3138	1788	3447	88(3)
Cl(310)	5769(2)	1819(2)	2669(2)	74(1)	4802(3)	3186(1)	6546(2)	59(1)
O(311)	6614	1879	2511	109(3)	4471	2987	7017	113(3)
O(312)	5139	2292	2532	116(3)	5065	3627	6678	127(4)
O(313)	6162	1603	3714	135(4)	4159	3109	5814	130(4)
O(314)	5130	1307	1786	126(3)	5860	2973	6734	190(7)
Cl(320)	6780(3)	1988(2)	7383(3)	70(1)	−77(2)	1302(1)	5035(2)	55(1)
O(321)	7759	1876	8037	92(3)	−1073	1130	4859	111(3)
O(322)	6408	2505	7807	128(5)	−62	1661	4665	101(3)
O(323)	6150	1604	7527	208(10)	753	995	5156	131(4)
O(324)	6441	1730	6334	222(10)	331	1443	5769	141(5)
Cl(330)	7044(3)	4759(1)	5807(3)	66(1)	9279(3)	1348(1)	1431(2)	74(1)
O(331)	6859	5371	6038	106(4)	10395	1453	1731	149(5)
O(332)	6511	4279	5184	131(4)	8500	1449	743	149(5)
O(333)	8136	4670	6507	134(5)	9315	903	1535	199(7)
O(334)	6913	4560	6786	205(9)	8974	1579	1745	209(8)
Cl(340)	8503(2)	4136(2)	1777(3)	61(2)				
O(341)	7769	4497	1508	188(9)				
O(342)	9407	4100	1763	238(11)				
O(343)	8706	4111	2873	146(6)				
O(344)	7884	3502	999	205(8)				

a) $B_{eq}=4/3\sum_i\sum_j \beta_{ij}\boldsymbol{a}_i\boldsymbol{a}_j$.

phenolate),[17] $(Et_3NH)_2[Ti(cat)_3]$ (1.97 Å; cat=catecholate), $K_4[TiO(cat)_2]_2\cdot 9H_2O$ (1.97 Å), and $(Et_3NH)_2$-$[TiH(dtbc)_3]\cdot 2CHCl_3$ (1.97 Å; dtbc=3,5-di-*t*-butylcatecholate).[18]

The bite angles of dam (av 91° for **1** and 93° for **2**) are much larger than those of catecholate (78—80°) forming a five-membered ring or acetylacetonate (83°) forming a six-membered ring.[16-18] The Ti atoms are located at various distances from six pyrazolone planes, 1.136, 1.128, 0.744, 0.341, 1.429, and 0.260 Å for **1** and 0.518, 0.542, 0.915, 0.283, 1.033, and 0.054 Å for **2**.

Ligand Conformation and Aromatic Ring Stacking. Chelate rings of medium size (eight- to eleven-membered rings) are known to be hardly formed

Table 3. Metal-Ligand Distances (Å) and Angles (°) with esd Values in Parentheses for **1** and **2**

Compound	1	2
Ti–O(6)	1.929(5)	1.888(7)
Ti–O(6′)	1.929(6)	1.922(7)
Ti–O(106)	1.930(5)	1.943(7)
Ti–O(106′)	1.938(6)	1.939(7)
Ti–O(206)	1.958(6)	1.976(7)
Ti–O(206′)	1.917(6)	1.958(7)
O(6)–Ti–O(6′)	89.3(2)	92.1(3)
O(6)–Ti–O(106)	89.8(2)	90.1(3)
O(6)–Ti–O(106′)	178.7(3)	178.0(3)
O(6)–Ti–O(206)	92.7(2)	92.9(3)
O(6)–Ti–O(206′)	90.2(2)	92.1(3)
O(6′)–Ti–O(106)	88.1(2)	91.0(3)
O(6′)–Ti–O(106′)	90.0(3)	89.3(3)
O(6′)–Ti–O(206)	174.9(3)	174.4(3)
O(6′)–Ti–O(206′)	90.9(3)	88.6(3)
O(106)–Ti–O(106′)	91.3(2)	91.3(3)
O(106)–Ti–O(206)	87.3(2)	86.3(3)
O(106)–Ti–O(206′)	179.0(3)	177.7(3)
O(106′)–Ti–O(206)	88.1(3)	85.8(3)
O(106′)–Ti–O(206′)	88.7(3)	86.5(3)
O(206)–Ti–O(206′)	93.7(3)	93.9(3)

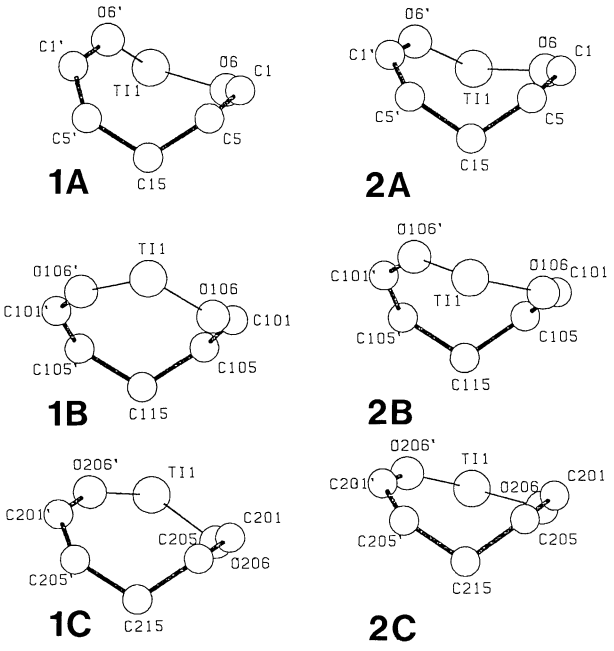

Fig. 3 Projection of the eight-membered chelate rings on the C(5)–C(15)–C(5′) planes.

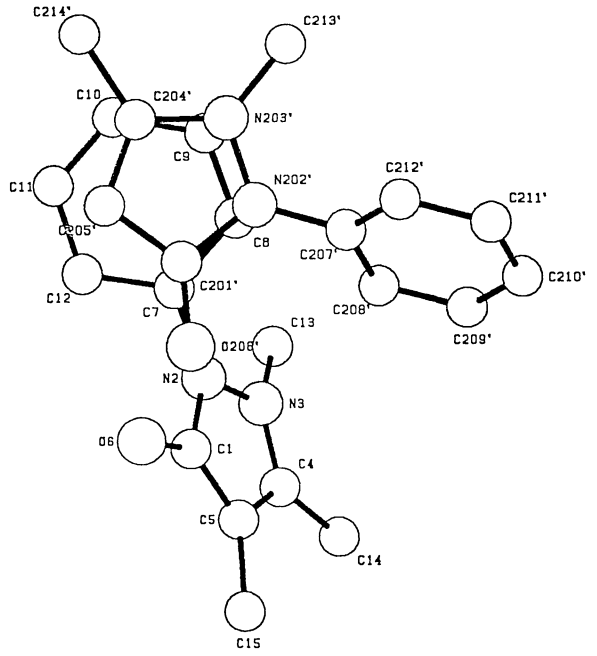

Fig. 4 Projection of the phenyl ring (Ⓟh of A) on the least squares plane of the pyrazolone moiety (Ⓟy of C) for **1**.

because of ring strain and entropy factor in the ring closure process.[11,12] In **1** and **2**, however, dam acts as a bidentate ligand to construct an eight-membered ring. It is partly because of the rigidity of this ligand; free rotation is possible only for C(5)–C(15) and C(5′)–C(15). Six eight-membered rings adopt varying conformation as shown in Fig. 3. Within a ligand, one pyrazolone moiety is almost perpendicular to the plane through C(5), C(15), and C(5′), whereas the other not. Dihedral angles between two pyrazolone moieties within a ligand are between 61.4—70.1° (av 65°) except ligand B of **1**, which has an exceptionally small value of 47.0°.

Another striking feature of these complexes is aromatic ring stacking between a pyrazolone moiety of one ligand and a phenyl ring of another. An example for **1** is shown in Fig. 4, and relationship between twelve rings is schematically presented in Fig. 5, together with the closest interatomic distances and dihedral angles between rings. To bring about this stacking, phenyl groups are not coplanar with pyrazolone moieties within a ligand as shown by dihedral angles(47.5—77.3°, av 60°) in Fig. 5.

It is evident that the stacking is more pronounced for the complex **1** than for **2**; for example, that between phenyl group of B and pyrazolone ring of C (Fig. 2). Such stacking not only facilitates the formation of eight-membered rings, but also contributes to the whole stability of these complexes.

Implication for the Coloration. When both crystals were suspended in 1 mol dm^{-3} hydrochloric acid solution, **1** was rapidly and **2** was slowly dissolved to give a solution having an absorption maximum at 385 nm, which agrees well with that of the species used for photometric determination of Ti(IV).

In the ternary systems of Cu–an aromatic amine–a nucleotide, a phenylalkanecarboxylate or an aromatic amino acid, a single well-defined absorption peak appears around 360 nm, which is ascribed to a CT

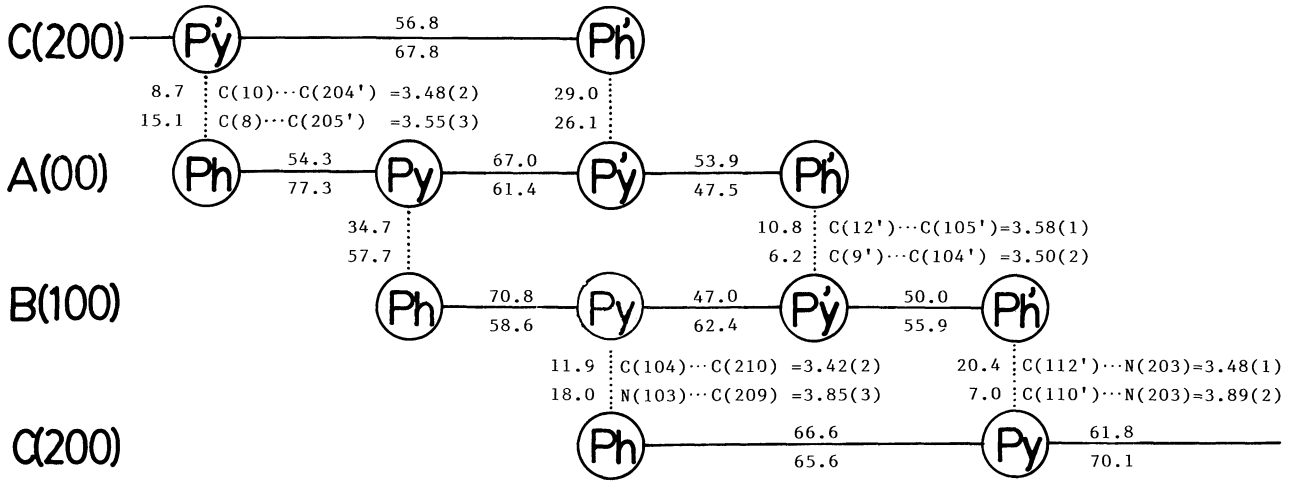

Fig. 5 Relationship between twelve aromatic rings. (Ph), (Ph'): phenyl group; (Py), (Py'): pyrazolone moiety. Solid line: covalent bond; dotted line: aromatic ring stacking. The closest interatomic distances are given for appreciable ring-overlapping. Other numbers are dihedral angles between two rings. Upper: **1**; lower: **2**.

band.[19–23] X-ray crystal structures just demonstrate the intramolecular aromatic ring stacking in Cu–phenanthroline–tryptophan.[24,25]

Since Ti-dam has several stacking of appreciable ring overlapping, the absorption band at around 385 nm is likewise assigned to a CT band. The electron flows from phenyl groups to pyrazolone moieties made electron-deficient by the coordination to Ti(IV) center.

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