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Octahedral Tantalum and Niobium Cluster Complexes with Chloro and Trialkylphosphine Ligands. Isolation and Structure Determination of the Trans and Cis Isomers

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Both trans and cis isomers of the octahedral tantalum clusters $[(Ta_6Cl_{12})Cl_2(PR_3)_4]$ ($R = C_2H_5$, C_3H_7, and C_4H_9) have been isolated by the column chromatography. Oxidation of these neutral isomers by $NOBF_4$ has yielded the trans and cis isomers of the mono- and dicationic complexes. No isomerization reaction was observed. Though the electronic spectra of the neutral isomers are almost identical, the trans and the cis isomers of $[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]^{n+}$ ($n = 1, 2$) show different absorption bands around 13×10^3 cm^{-1}, which indicates the splitting of a metal cluster orbital (t_{1u} or t_{2g}) due to the lowering of the symmetry from O_h. For the niobium derivatives, only the trans isomers have been obtained. The structures of the following complexes have been determined by the X-ray diffraction method. Crystallographic data: *trans*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]\cdot CHCl_3$, *Pbca*, $a = 21.974$ (6) Å, $b = 22.603$ (7) Å, $c = 12.099$ (2) Å, $Z = 4$; *trans*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4][BF_4]\cdot CHCl_3$, $P2_1/a$, $a = 19.874$ (3) Å, $b = 15.595$ (2) Å, $c = 10.019$ (2) Å, $\beta = 93.47$ (2)°, $Z = 2$; *cis*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4][BF_4]\cdot 3CH_2Cl_2$, $P2_1/m$, $a = 16.888$ (4) Å, $b = 16.141$ (5) Å, $c = 12.045$ (2) Å, $\beta = 93.88$ (2)°, $Z = 2$; *trans*-$[Nb_6Cl_{14}\{P(C_4H_9)_3\}_4]$, $P\bar{1}$, $a = 15.923$ (2) Å, $b = 20.881$ (3) Å, $c = 12.311$ (2) Å, $\alpha = 92.53$ (1)°, $\beta = 106.47$ (1)°, $\gamma = 90.22$ (1)°, $Z = 2$. The bond distances between the metals in the cluster depend not only on the oxidation state of the cluster but also on the kind of the terminal ligands on each metal.

Introduction

In the niobium and tantalum cluster complexes $[(M_6X_{12})Y_6]^{n+}$ (X = edge-bridging halogen; Y = terminal ligand), the bridging halo ligands are usually much less labile than the terminal ligands, and the inner core of the cluster complex, $(M_6X_{12})^{m+}$, may be regarded as a big pseudometal with six ligands. Therefore, just as in the chemistry of the mononuclear octahedral complexes, the geometric isomers of such cluster complexes should exist if they have more than two kinds of terminal ligands. However, no pair of such geometric isomers has been reported.[1] If such a pair of the isomers can be isolated, their comparison will reveal the effects of the terminal ligands on the structure and electronic states of the metal cluster.

The preparations of $[(M_6Cl_{12})Cl_2L_4]^{n+}$ (M = Nb, Ta; L = trialkylphosphines; $n = 0, 1, 2$) have been already reported by Klendworth and Walton.[2] In the present study, we have isolated the trans and cis isomers of these clutser complexes and have determined their structures. Here, the notation of "trans" and "cis" refers to the positions of the terminal chloro ligands on the apices of the metal octahedron. As expected, we have found differences in the electronic spectra between the trans and cis isomers, and they have given information about the assignments of the absorption bands of the tantalum clusters, which have been disputed for a long time.[3-6] In addition, the structural determinations of these complexes have revealed that the distortions of the metal octahedra of the trans and the cis isomer are different.

Experimental Section

Preparation. Though the preparative methods of the cluster phosphine complexes were basically similar to those in the literature,[2] we have modified them to obtain the pure isomers as described below.

The niobium and tantalum cluster hydrates, $M_6Cl_{14}\cdot 8H_2O$, were prepared[7] from metal powder (Nb, 99.9%, 325 mesh; Ta, 99.9%, 325 mesh) and the pentachlorides, which were obtained from the direct reaction of the elements. $NOBF_4$ (95%) was purchased from Alfa Products. Trialkylphosphines were partly prepared according to the literature,[8] and the rest of them were from Nippon Chemical Co. Ltd. All reactions were carried out under a dinitrogen or an argon atmosphere in the solvents distilled over the drying agents (P_2O_5 for CH_2Cl_2, $CHCl_3$, and CH_3CN; Na for benzene and toluene; NaOEt for ethanol). Column chromatography and recrystallization for the X-ray measurements were performed in air. For each column chromatography run, a solution of 3-5 g of the sample was applied on the column (3 cm in diameter) and eluted without pressure.

Measurements. ^{31}P NMR spectra were measured by a JEOL FX100 spectrometer with H_3PO_4 (85%) as external reference. Infrared spectra 400-50 cm^{-1}) were recorded on a Hitachi FIS spectrometer. Electronic spectra were obtained by use of a Hitachi 220A spectrometer for the range 300-900 nm and by use of a Hitachi U-3400 spectrometer for the range 380-1400 nm. Cyclic voltammograms were measured in CH_2Cl_2 solutions containing tetrabutylammonium perchlorate as supporting electrolyte with a platinum working electrode and a reference saturated calomel electrode. The scan rate was 100 mV/s, and the range was from +1.8 to -1.7 V.

In the following description of the spectral characterization, the values of λ_{max} in nm were written with log (ϵ_{max}/cm^{-1} mol^{-1} dm^3) given in parentheses for electronic spectra. The values of the IR data were expressed in units of cm^{-1}, and intensities of the peaks were classified in three groups: strong (s), medium (m), and weak (w). Shoulder peaks were designated as (sh).

***trans*- and *cis*-$[(Ta_6Cl_{12})Cl_2\{P(C_2H_5)_3\}_4]$ (1 and 2).** The tantalum chloride $Ta_6Cl_{14}\cdot 8H_2O$ (20.0 g, 11.6 mmol) was stirred with excess triethylphosphine (20.9, 177 mmol) in ethanol (650 mL) at room temperature for a week. The resulting solution with dark green precipitate was concentrated to half volume, cooled at 0 °C, and filtered. The solvent of the filtrate was removed under reduced pressure. The products obtained from the filtrate and from the precipitate were treated separately because the product from the filtrate contained the cis isomer in a higher ratio than the product from the precipitate. After being dried in vacuo, the product was washed with ether (20 mL × 4) and hexane (20 mL × 2) to yield a dark green powder (6.6 g from the precipitate and 17.2 g from the filtrate). The powder was dissolved in $CHCl_3$ and chromatographed on a Florisil column (40 cm long) with $CHCl_3$-ethanol (98:2) as eluent. The first eluted fractions gave **1** (yield: 1.8 g from the precipitate, 6.9 g from the filtrate, and 37% in total) and the third gave

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(1) There has been no report on the isolation of a pair of the geometric isomers of the halogeno clusters of niobium, tantalum, molybdenum, and tungsten. However, ^{31}P NMR studies of the alkyl molybdenum cluster complexes $[(Mo_6Cl_8)Cl_mR_{4-m}L_2]$ ($m = 1$-4, L = trialkylphosphines) have indicated the existence of many isomers in solution: Saito, T.; Nishida, M.; Yamagata, T.; Yamagata, Y.; Yamaguchi, Y.; *Inorg. Chem.* **1986**, *25*, 1111.

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2 (yield: 0.3 g from the precipitate, 3.4 g from the filtrate, and 16% in total). The second eluted fraction was presumed to be $[(Ta_6Cl_{12})X_3\{P(C_2H_5)_3\}_3]$ (X = Cl or OC_2H_5) from IR spectroscopy and elemental analysis. Both isomers were recrystallized from $CHCl_3$–heptane to yield green crystals. Anal. Calcd for $C_{24}H_{60}Cl_{14}P_4Ta_6$: C, 14.03; H, 2.94; Cl, 24.16. Found for **1**: C, 14.10; H, 2.93; Cl, 23.74. Found for **2**: C, 14.04; H, 2.92; Cl, 23.88. Electronic spectral data ($CHCl_3$): **1**, 235 (4.4), 275 (sh), 337 (4.4), 407 (3.6), 475 (sh), 683 (3.8), 806 (3.5); **2**, 235 (4.4), 275 (sh), 338 (4.4), 406 (3.6), 475 (sh), 681 (3.8), 809 (3.5). IR: **1**, 323 s, 317 s, 282 m, 240 m, 190 w, 152 w; **2**, 320 s, 281 s, 239 m, 190 w, 152 w. ^{31}P NMR: **1**, δ −4.70; **2**, δ −4.74, −5.07. Cyclic voltammetry ($E_{1/2}$): **1**, 0.24, 0.78 V; **2**, 0.23, 0.75 V. Solubility in 100 g of solvent: in acetone, **1**, 0.077 g, **2**, 0.24 g; in THF, **1**, 0.24 g, **2**, 1.5 g; in toluene, **1**, 0.047 g, **2**, 0.19 g.

***trans*- and *cis*-$[(Ta_6Cl_{12})Cl_2\{P(C_3H_7)_3\}_4]$ (3 and 4).** These compounds were prepared from $Ta_6Cl_{14}\cdot 8H_2O$ (4.43 g, 2.57 mmol) and tripropylphosphine (6.30 g, 39.3 mmol) by the same procedure described for the synthesis of **1** and **2** except that CH_2Cl_2–ethanol solution (98:2) was used as eluent. Both compounds were green. Yield: 1.94 g (34%) of **3** and 1.26 g (22%) of **4**. The trans isomer is poorly soluble in $CHCl_3$ in contrast with other neutral complexes. Anal. Calcd for $C_{36}H_{84}Cl_{14}P_4Ta_6$: C, 19.45; H, 3.81; Cl, 22.33. Found for **3**: C, 19.49; H, 3.75; Cl, 21.95. Found for **4**: C, 19.20; H, 3.69; Cl, 22.49. Electronic spectral data ($CHCl_3$): **3**, 244 (4.3), 275 (sh), 337 (4.4), 337 (4.4), 406 (3.6), 475 (sh), 686 (3.8), 810 (3.5). IR: **3**, 323 s, 282 m, 240 m, 192 w, 154 w; **4**, 322 s, 280 s, 239 m, 194 w, 150 w. ^{31}P NMR: **3**, δ −10.36; **4**, δ −10.32, −10.76. Cyclic voltammetry ($E_{1/2}$): **3**, 0.24, 0.80 V; **4**, 0.25, 0.75 V.

***trans* and *cis*-$[(Ta_6Cl_{12})Cl_2\{P(C_4H_9)_3\}_4]$ (5 and 6).** These compounds were prepared from $Ta_6Cl_{14}\cdot 8H_2O$ (6.00 g, 3.48 mmol) and tributylphosphine (10.49 g, 51.9 mmol) by the same procedure as described for the synthesis of **1** and **2**. Yield: 2.83 g (34%) of **5** and 1.08 g (13%) of **6**. Anal. Calcd for $C_{48}H_{108}Cl_{14}P_4Ta_6$: C, 24.11; H, 4.55; Cl, 20.76. Found for **5**: C, 24.03; H, 4.54; Cl, 20.83. Found for **6**: C, 24.09; H, 4.47; Cl, 20.46. Electronic spectral data ($CHCl_3$): **5**, 240 (4.3), 275 (sh), 337 (4.4), 407 (3.6), 475 (sh), 682 (3.8), 810 (3.5); **6**, 240 (4.4), 275 (sh), 337 (4.4), 406 (3.6), 475 (sh), 685 (3.8), 811 (3.5). IR: **5**, 318 s, 282 m, 240 m, 192 w, 151 w; **6** 330 m (sh), 321 s, 280 m, 238 m, 191 w, 150 w. ^{31}P NMR: **5**, δ −10.61; **6**, δ −10.50, −10.90.

***trans*-$[(Nb_6Cl_{12})Cl_2\{P(C_2H_5)_3\}_4]$ (7).** Triethylphosphine (4.9 g, 41 mmol) was added to a solution of $Nb_6Cl_{14}\cdot 8H_2O$ (7.7 g, 6.5 mmol) in ethanol (300 mL). The solution was stirred for 2 days, and refluxed for 2 days. The solvent was then removed in vacuo and the residue was washed with ether (4 × 40 mL). The product was purified by column chromatography on silica gel (30 cm long) with $CHCl_3$–ethanol (98:2) as eluent and washed with ether. Yield: 2.3 g (37%) of olive green crystals. Anal. Calcd for $C_{24}H_{60}Cl_{14}Nb_6P_4$: C, 18.89; H, 3.96; Cl, 32.52. Found: C, 19.14; H, 3.86; Cl 31.94. IR: 345 (sh), 340 s, 295 s, 276 m, 249 m, 237 m, 207 w, 132 w, 120–105 w. Electronic spectral data ($CHCl_3$): 265, 412, 612, 942. ^{31}P NMR ($CHCl_3$): δ 7.70.

***trans*-$[(Nb_6Cl_{12})Cl_2\{P(C_3H_7)_3\}_4]$ (8).** This compound was prepared from $Nb_6Cl_{14}\cdot 8H_2O$ (5.9 g, 4.9 mmol) and tripropylphosphine (12.6 g, 78.6 mmol) by the same procedure described for the synthesis of **7** except that it was purified by column chromatography on Florisil with ethanol–$CHCl_3$ (2:98) as eluent. Yield: 2.6 g (31%) of olive green crystals. Anal. Calcd for $C_{36}H_{84}Cl_{14}Nb_6P_4$: C, 25.51; H, 5.00. Found: C, 25.33; H, 4.91. Electronic spectral data ($CHCl_3$): 265, 412, 612, 942. ^{31}P NMR ($CHCl_3$): δ 1.97.

***trans*-$[(Nb_6Cl_{12})Cl_2\{P(C_4H_9)_3\}_4]$ (9).** Tributylphosphine (10.3 mL, 4.1 mmol) was added to a solution of $Nb_6Cl_{14}\cdot 8H_2O$ (9.8 g, 8.3 mmol) in ethanol (300 mL). The solution was refluxed for 1 day and stirred for 2 days. The solvent was removed in vacuo and the residue was washed with ether (3 × 40 mL) and hexane (3 × 20 mL). Purification by column chromatography on silica gel with ethanol–$CHCl_3$ (99:1) as eluent yielded olive green crystals of **9** (5.8 g, 37%). Anal. Calcd for $C_{48}H_{108}Cl_{14}Nb_6P_4$: C, 30.95; H, 5.84. Found: C, 30.87; H, 5.87. Electronic spectral data ($CHCl_3$): 259, 411, 610, 950. ^{31}P NMR ($CHCl_3$): δ 1.87.

***trans*-$[(Ta_6Cl_{12})Cl_2\{P(C_2H_5)_3\}_4][BF_4]$ (10).** A solution of $NOBF_4$ in CH_3CN (0.1 mol/dm^3, 4.9 mL) was added dropwise to a suspension of **1** (0.47 g, 0.23 mmol) in CH_3CN (30 mL) until no neutral complex was detected with TLC (silica gel). As the reaction proceeded, the suspension became an orange solution. The solvent was removed in vacuo, and the residue was washed with $CHCl_3$ (20 mL) and ether (2 × 20 mL). Yield: 0.40 g (82%). The product was recrystallized from CH_3CN–ether to give orange crystals, which were stable in air. The complex was prepared also by the oxidation with $AgBF_4$ instead of $NOBF_4$. In this case, the procedure was similar to that described above except that silver metal was removed by careful filtration after the reaction. Anal. Calcd for $C_{24}H_{60}BCl_{14}F_4P_4Ta_6$: C, 13.46; H, 2.82. Found: C, 13.42; H, 2.78. Electronic spectral data (CH_2Cl_2): 275 (sh), 345 (4.3), 410 (sh), ca. 500 (sh), 746 (3.3), 780 (3.3), 833 (3.3), 960 (3.3). IR: 331 s, 292 s, 254 m, 184 w, 150 w, 144 w. Solubility in 100 g of solvent: acetone, 1.2 g; THF, 0.02 g; $CHCl_3$, 0.04 g.

***cis*-$[(Ta_6Cl_{12})Cl_2\{P(C_2H_5)_3\}_4][BF_4]$ (11).** A solution of $NOBF_4$ in CH_3CN (0.1 M, 3.4 mL) was added dropwise to a solution of **2** (0.338 g, 0.165 mmol) in CH_3CN (20 mL) until no neutral complex was detected with TLC. The color of the solution changed from green to orange as $NOBF_4$ was added. The solvent was then removed in vacuo. The residual oil as washed with toluene, dried in vacuo, washed with ether, and dried again in vacuo to yield an orange powder. Recrystallization from CH_3CN solution afforded orange crystals of **11** (0.26 g, 73%). The complex was prepared also by oxidation with $AgBF_4$ instead of $NOBF_4$. Anal. Calcd for $C_{24}H_{60}BCl_{14}F_4P_4Ta_6$: C, 13.46; H, 2.82. Found: C, 13.34; H, 2.64. Electronic spectral data (CH_2Cl_2): 275 (sh), 344 (4.4), 412 (sh), ca. 500 (sh), 770 (3.5, br). IR: 330 s, 290 s, 270 m, 248 m, 182 w, 150 w, 144 w. Solubility in 100 g of solvent: acetone, 8.1 g; THF, 1.4 g; $CHCl_3$, 3.2 g.

***trans*-$[(Ta_6Cl_{12})Cl_2\{P(C_3H_7)_3\}_4][BF_4]$ (12).** The compound was prepared from **3** by the same procedure as described for the synthesis of **10**. The product was washed with toluene and ether. Anal. Calcd for $C_{36}H_{84}BCl_{14}F_4P_4Ta_6$: C, 18.72; H, 3.67. Found: C, 18.67; H, 3.59. IR: 331 s, 291 s, 252 m, 187 w, 149 w.

***cis*-$[(Ta_6Cl_{12})Cl_2\{P(C_3H_7)_3\}_4](BF_4]$ (13).** The compound was prepared from **4** (0.124 g, 0.056 mmol) by the same procedure as described for the synthesis of **11**. Yield: 0.075 g, 58%. Anal. Found: C, 18.13; H, 3.42. IR: 330 s, 292 m, 287 m (sh), 247 m, 197 w, 187 w, 148 w.

***trans*-$[(Ta_6Cl_{12})Cl_2\{P(C_2H_5)_3\}_4][BF_4]_2$ (14).** A solution of $NOBF_4$ in CH_3CN (0.1 M, 5.2 mL) was added to a suspension of **1** (0.15 g, 0.074 ml) in CH_3CN (20 mL). As the reaction proceeded, the suspension became an orange solution and then a red-orange solution. The solvent was removed in vacuo, and the residue was washed with ethanol (2 × 20 mL) and ether (2 × 20 mL). Yield: 0.14 g (82%). The product was recrystallized from CH_3CN–ether. The compound was brown and stable in air. It was very easily reduced in solution. Anal. Calcd for $C_{24}H_{60}B_2Cl_{14}F_8P_4Ta_6$: C, 12.94; H, 2.71. Found: C, 13.52; H, 2.67. Electronic spectral data (CH_3CN): 353 (4.4), 421 (sh), 500 (sh), 680 (2.8), 774 (3.2). IR: 342 s, 303 m, 270 m, 149 w, 85–50 w.

***cis*-$[(Ta_6Cl_{12})Cl_2\{P(C_2H_5)_3\}_4][BF_4]_2$ (15).** A solution of $NOBF_4$ in CH_3CN (0.1 M, 4.6 mL) was added to a suspension of **2** (0.14 g, 0.066 mmol) in CH_3CN (20 mL). The solvent was removed in vacuo, and the residue was washed with ethanol–ether (1:1). Yield: 0.09 g (62%). The compound was brown and stable in air. Because the compound was soluble in alcohols and reduced by them, it was difficult to remove the unreacted $NOBF_4$ without partial reduction of **15**. The electronic spectrum of the product always showed some contamination with monocationic species. Anal. Calcd for $C_{24}H_{60}B_2Cl_{14}F_8P_4Ta_6$: C, 12.94; H, 2.71. Found: C, 12.79; H, 2.61. Electronic spectral data (CH_3CN): 353 (4.4), 424 (sh), 500 (sh), 734 (3.1, br). IR: 341 s, 302 m, 265 m, 233 w, 180 w, 145 w, 90–50 w.

Structure Determination. The crystals of the tantalum complexes for X-ray studies, which contained solvent molecules, were sealed in a capillary while the crystal of the niobium complex was fixed on the top of a glass rod with adhesive. The possible space groups and the approximate cell constants of the crystals studied in this work were determined by the oscillation, Weissenberg, and precession photographs. The reflection data and the data for the accurate cell constants were measured with a Rigaku AFC-4 diffractometer equipped with a Rotaflex rotating anode X-ray generator with the Mo Kα radiation monochromatized with graphite (wavelength: 0.71069 Å) at the Protein Engineering Research Center, Osaka University. The reflection data of all crystals were corrected for the *Lp* factor, and did not indicate any decay. An empirical absorption correction was applied for the reflection data of all tantalum complexes.

The positions of the heavy atoms (Ta, Nb, Cl, and P) in the cluster units were determined by direct methods (MULTAN78), and other non-hydrogen atoms were located in the successive Fourier maps. A new program, ANYBLK, was used for the refinements,[9] and all structures were refined by the full-matrix least-squares method. In the final stages of refinements, hydrogen atoms were placed at 1.08 Å from carbon atoms. The positions of methyl hydrogen atoms were determined so that the dihedral angle of H–C–C–P (or C) would become 60 + 120n° (n = 0–2).

The neutral-atom scattering factors in the analytical form were used in the calculation, and anomalous dispersion effects were included in F_c.[10] The calculations were performed on an NEC ACOS S930 computer at the Protein Engineering Research Center, Osaka University.

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[9] This program was written by H. Imoto for the refinement of the structures in this work. It uses the usual algorithm for the least-squares refinement. It can refine structures by keeping any kind of linear relations between the parameters to be refined and also the shapes of any groups of the atoms as rigid bodies with or without the conditions of constrained movement. The sizes of the refinement blocks can be changed freely between block-diagonal and full-matrix refinement.

Table I. Crystal Parameters and X-ray Diffraction Data[a]

	1a	**10a**	**11a**	**9**
formula	$C_{24}H_{60}Cl_{14}P_4Ta_6\cdot CHCl_3$	$C_{24}H_{60}Cl_{14}BF_4P_4Ta_6\cdot CHCl_3$	$C_{24}H_{60}Cl_{14}BF_4P_4Ta_6\cdot(CH_2Cl_2)_3$	$C_{48}H_{108}Cl_{14}Nb_6P_4$
fw	1541.12	1916.27	2151.82	2526.97
space group	*Pbca*	$P2_1/a$	$P2_1/m$	$P\bar{1}$
a/Å	21.974 (6)	19.874 (3)	16.888 (4)	15.923 (2)
b/Å	22.603 (7)	15.595 (2)	16.141 (5)	20.881 (3)
c/Å	12.099 (2)	10.019 (2)	12.045 (2)	12.311 (2)
β/deg		93.47 (2)	93.88 (2)	106.47 (1)[d]
cell vol/Å^3	6009 (2)	3100 (1)	3276 (1)	3921 (1)
Z	4	2	2	2
no. of used reflcn[b]	4293, $>4\sigma$	5033, $>3\sigma$	4069, $>4\sigma$	8902, $>6\sigma$
$R(F_o)$, $R_W(F_o^2)$[c]	0.046, 0.039	0.042, 0.032	0.052, 0.044	0.48, 0.052

[a] All X-ray data were measured at 20 °C. [b] The number of the observed reflections used for the refinement and the cutoff condition. [c] $w = 1/\sigma^2(F_o)$ [d] $\alpha = 92.53\ (1)°$; $\gamma = 90.22\ (1)°$.

***trans*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]\cdot CHCl_3$ (1a).** The observed systematic absences unequivocally determined the space group to be *Pbca*. The heavy atoms of the cluster molecule (Ta, Cl, and P) were refined anisotropically, and other non-hydrogen atoms were refined isotropically. The isotropic temperature factors of all hydrogen atoms were set equal and refined as one parameter. Positional parameters of hydrogen atoms were not refined.

The crystal for X-ray measurements was recrystallized from a CH_2Cl_2–pentane solution. However, the structure determination revealed that the solvent molecules in the crystal were $CHCl_3$.[11] The $CHCl_3$ molecule was believed to have been introduced with the container, which might have been washed with $CHCl_3$ before use. Since the $CHCl_3$ molecule seemed to fit in the space of the crystal lattice better than the CH_2Cl_2 molecule, it was not improbable that the small amount of $CHCl_3$ was concentrated in the good crystals. The very low yield of the good crystals also supported the assumption. More than 100 crystals had been examined by X-ray photographs before a good single crystal was obtained.

***trans*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4][BF_4]\cdot CHCl_3$ (10a).** The observed systematic absences unequivocally determined the space group to be $P2_1/a$. All non-hydrogen atoms were refined anisotropically. The dihedral angles of H–C–C–P were refined by treating the methyl groups as rigid bodies with freedom to rotate around the C–C bonds. All of the isotropic thermal parameters of hydrogen atoms were set equal and refined as one parameter.

The crystal for X-ray measurements were recrystallized from a CH_2Cl_2–pentane solution, but the structure determination showed that the solvent in the crystal was $CHCl_3$.[12] We think the reason was the same as that described for the solvent in **1a**.

***cis*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4][BF_4]\cdot 3CH_2Cl_2$ (11a).** The crystal for the X-ray measurements was obtained by recrystallization from a CH_2Cl_2–heptane solution. If the space group $P2_1$ was assumed, the refinements did not converge. Therefore, the only possible space group consistent with the observed systematic absences was the centrosymmetric group $P2_1/m$. The Ta, Cl, and P atoms in the cluster cations were refined anisotropically, and other non-hydrogen atoms were refined isotropically. The positional parameters and the isotropic temperature factors of the hydrogen atoms were fixed. The $[BF_4]^-$ ions and the CH_2Cl_2 molecules are located in the large tunnels running along the b axis and are loosely bound in the structure. These species were treated as rigid bodies because refinements in the usual full-matrix method resulted in deformed shapes. The $[BF_4]^-$ ion was assumed to be a tetrahedron with B–F bonds of 1.37 Å. The length C–Cl and Cl–C–Cl angles in the CH_2Cl_2 molecules are fixed at 1.77 Å and 109.47°, respectively. The $[BF_4]^-$ ion was located at the inversion center, and disordered in two orientations that were related by the inversion symmetry. The isotropic thermal parameters of all fluorine atoms of the $[BF_4]^-$ ion were set equal. The structure had two kinds of CH_2Cl_2 molecules. The first molecule was located near the mirror plane and, therefore, was disordered in two positions overlapping partly with each other. The second CH_2Cl_2 molecule was found in a large space and showed very large thermal parameters. The occupation factors of the both molecules were refined to be a little smaller than the possible highest values, 0.5 and 1.0, respectively (see Table IV).

***trans*-$[Nb_6Cl_{14}\{P(C_4H_9)_3\}_4]$.** The crystal for the X-ray study was obtained by the recrystallization from a toluene–acetone solution. The structure was successfully solved when the centrosymmetric group $P\bar{1}$ was assumed. The heavy atoms (Nb, Cl, and P) were refined anisotropically, and the carbon atoms were refined isotropically. The hydrogen atoms with isotropic temperature factors were not refined. This normal refinement converged to give a reasonably low R value. However, among the 36 C–C bonds, two bonds were abnormally short (1.03 and 1.06 Å) and two bonds were long (both 1.85 Å). Refinement with the space group $P1$ did not improve the anomaly. This anomaly and the large thermal parameters of methyl carbon atoms (i.e. the end of the butyl chain) suggested that the positions of the butyl groups were disordered among a number of sites. In order to examine the influence of the locations of the butyl groups on the refined bond distances between the atoms in the cluster, we refined the structure also under the constraint that the butyl chains were held in the normal shape (C–C = 1.54 Å, P–C = 1.85 Å, angle C–C–C (or P) = 109.47°). This refinement gave slightly higher R values ($R(F_o) = 0.055$, $R_w(F_o^2) = 0.066$). Though the positions of the carbon atoms deviated from the result of the normal refinement by as much as 0.32 Å, the bond distances between heavy atoms (Nb, Cl, and P) were not significantly changed. The largest differences of the bond lengths between the two refinements were 0.001 Å for Nb–Nb, 0.003 Å for Nb–Cl, and 0.004 Å for Nb–P. Therefore, we concluded that both refinements were reliable for the discussion of the structure of the cluster, and we will present the results obtained by the normal refinement.

Results

Preparation and Characterization. We could isolate both the trans and cis isomers of the tantalum cluster complexes as described in the Experimental Section. The compounds reported by Klendworth and Walton as $[Ta_6Cl_{14}\{P(C_3H_5)_3\}_4]^{n+}$ (n = 0–2) appear to contain mainly the trans isomers because the reported electronic spectra of the oxidized species are similar to those of the trans complexes.

The trans and the cis isomers had different solubilities in organic solvents. In general, the cis isomer was more soluble than the trans (see Experimental Section). For example, the monocationic cis isomers of the tripropylphosphine complex dissolved in chloroform, and the trans did not. When chromatographed, the neutral cis isomer was more strongly adsorbed due to its higher polarity than that of the corresponding trans isomer.

The trans and the cis isomers with the same charge had similar color. The trans and cis isomers showed identical IR spectra in the region 4000–350 cm^{-1}, where the absorptions are due to the coordinating trialkylphosphines. Distinct differences were observed in the far-infrared spectra (400–50 cm^{-1}) between the trans and cis isomer (see Experimental Section). However, the spectra depended not only on the geometry but also on the kind of the phosphines and on the oxidation state of the cluster, and we could not discern any systematic difference between the trans and cis isomers. The electronic spectra (200–1400 nm) of the neutral isomers were also similar, but those of the isomers of the oxidized cluster had obvious differences in the region 600–1200 nm (vide infra).

The cyclic voltammetry of the neutral complexes showed that the first oxidation potentials of the trans and cis isomers were the same within the experimental error. However, the second oxidation potential of the trans isomer was slightly higher than that of the cis isomer (ca. 0.04 V; see Experimental Section).

The cis and trans isomers of the neutral complex could be clearly

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(10) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. (b) Cromer, D. T. *Ibid.*, Table 2.3.1.

[11] The refined occupation factors of the chlorine atoms of the chloroform molecule were 0.98 (3), 0.92 (2), and 0.99 (3).

[12] The refined occupation factors of the chlorine atoms of the chloroform molecule were 1.01 (2), 0.99 (2), and 0.92 (2).

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for *trans*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]\cdot CHCl_3$

atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	$U_{eq}/10^{-3}$ Å^2
Ta(1)	380.9 (2)	627.2 (3)	-1037.0 (4)	27.2 (3)
Ta(2)	-843.7 (2)	199.2 (3)	-600.8 (4)	27.0 (3)
Ta(3)	-103.0 (2)	627.2 (3)	1200.9 (4)	26.1 (3)
Cl(1)	-561 (1)	965 (2)	-1947 (3)	42 (2)
Cl(2)	331 (1)	1483 (2)	223 (3)	40 (2)
Cl(3)	1453 (1)	500 (2)	-510 (3)	38 (2)
Cl(4)	586 (1)	-17 (2)	-2632 (3)	36 (2)
Cl(5)	-1125 (1)	990 (2)	706 (3)	39 (2)
Cl(6)	-880 (1)	-508 (2)	-2154 (3)	37 (2)
Cl(7)	848 (2)	1394 (2)	-2303 (3)	47 (2)
Cl(8)	2293 (3)	2992 (4)	4622 (9)	188 (9)
Cl(9)	1377 (2)	2246 (3)	5464 (6)	104 (5)
Cl(10)	1859 (4)	2047 (4)	3319 (7)	159 (8)
P(1)	-1996 (2)	450 (2)	-1328 (3)	42 (2)
P(2)	-249 (2)	1446 (2)	2846 (3)	39 (2)
C(1)	-2098 (10)	1081 (11)	-2221 (24)	107 (20)
C(2)	-1986 (10)	1658 (17)	-1626 (30)	169 (32)
C(3)	-2352 (6)	-90 (10)	-2264 (13)	69 (13)
C(4)	-2465 (7)	-693 (9)	-1730 (18)	78 (14)
C(5)	-2534 (6)	519 (8)	-188 (12)	52 (10)
C(6)	-3210 (6)	559 (9)	-496 (17)	70 (13)
C(7)	-43 (8)	2229 (8)	2554 (15)	62 (11)
C(8)	-490 (9)	2520 (9)	1723 (18)	90 (15)
C(9)	205 (7)	1357 (9)	4112 (14)	60 (12)
C(10)	80 (9)	791 (9)	4806 (15)	81 (15)
C(11)	-1034 (7)	1495 (9)	3313 (16)	70 (13)
C(12)	-1147 (8)	1898 (12)	4344 (20)	117 (20)
C(13)	1679 (8)	2577 (10)	4298 (21)	93 (17)

Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters for *trans*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4][BF_4]\cdot CHCl_3$

atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	$U_{eq}/10^{-3}$ Å^2
Ta(1)	-737.1 (2)	-165.2 (3)	1399.9 (4)	24.4 (2)
Ta(2)	-470.0 (2)	-919.9 (3)	-1211.0 (4)	23.3 (2)
Ta(3)	582.3 (2)	-947.1 (3)	946.0 (4)	23.3 (2)
Cl(1)	-1410 (1)	-1253 (2)	169 (3)	33 (1)
Cl(2)	-160 (1)	-1285 (2)	2740 (3)	33 (1)
Cl(3)	-284 (1)	876 (2)	3046 (3)	36 (1)
C6(4)	-1524 (1)	931 (2)	511 (3)	35 (1)
Cl(5)	111 (1)	-2182 (2)	-280 (3)	32 (1)
Cl(6)	-1232 (1)	32 (2)	-2526 (3)	34 (1)
Cl(7)	-1618 (1)	-378 (2)	3040 (3)	46 (2)
Cl(8)	1312 (4)	4652 (4)	6142 (6)	163 (5)
Cl(9)	1229 (2)	3099 (3)	7587 (5)	86 (3)
Cl(10)	2018 (2)	4487 (3)	8669 (5)	95 (3)
P(1)	-1052 (2)	-2176 (2)	-2773 (3)	35 (2)
P(2)	1329 (1)	-2227 (2)	2155 (3)	32 (1)
C(1)	-1739 (7)	-1835 (9)	-3952 (14)	61 (9)
C(2)	-2385 (7)	-1598 (10)	-3332 (16)	79 (10)
C(3)	-1401 (6)	-3049 (7)	-1788 (12)	46 (7)
C(4)	-1722 (7)	-3793 (8)	-2595 (15)	67 (9)
C(5)	-508 (7)	-2703 (8)	-3931 (13)	53 (8)
C(6)	92 (7)	-3210 (9)	-3350 (16)	71 (10)
C(7)	1974 (6)	-2734 (7)	1165 (13)	45 (7)
C(8)	1699 (7)	-3217 (8)	-78 (14	60 (9)
C(9)	808 (6)	-3114 (7)	2672 (13)	47 (7)
C(10)	1188 (7)	-3883 (8)	3331 (15)	65 (9)
C(11)	1847 (6)	-1930 (7)	3661 (11)	41 (6)
C(12)	1450 (6)	-1701 (8)	4867 (12)	49 (7)
C(13)	1299 (7)	4212 (10)	7706 (14)	63 (9)
B	5000	0	0	71 (18)
F(1)	5155 (13)	831 (11)	-210 (25)	94 (14)
F(2)	5398 (17)	-509 (16)	-632 (34)	154 (25)
F(3)	4325 (11)	-148 (23)	-390 (25)	132 (20)
F(4)	5076 (12)	-123 (18)	1406 (25)	123 (19)

distinguished by their ^{31}P NMR spectra. While the trans isomer has only one kind of phosphine ligand, the cis isomer has two kinds of phosphine ligands: two phosphines are trans to each other, and the other two are trans to the chloro ligands. For example, the observed ^{31}P NMR spectrum of *cis*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]$ had two signals at δ -4.74 and -5.07 with equal intensities while the trans isomer had one signal at δ -4.70.

Table IV. Positional Parameters and (Equivalent) Isotropic Thermal Parameters[a] for *cis*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4][BF_4]\cdot 3CH_2Cl_2$[b]

atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	$U_{eq}/10^{-3}$ Å^2
Ta(1)	3688.2 (4)	3417.6 (5)	-940.6 (6)	33.9 (4)
Ta(2)	4714.0 (6)	2500	702.4 (10)	29.7 (6)
Ta(3)	2311.0 (6)	2500	-212.7 (10)	32.0 (6)
Ta(4)	3340.2 (4)	3407.7 (5)	1426.8 (6)	28.8 (4)
Cl(1)	3922 (4)	2500	-2493 (6)	51 (5)
Cl(2)	5121 (2)	3565 (3)	-579 (4)	46 (3)
Cl(3)	2305 (3)	3558 (3)	-1652 (4)	47 (3)
Cl(4)	3496 (3)	4619 (2)	264 (5)	44 (2)
Cl(5)	4718 (2)	3568 (3)	2134 (4)	39 (3)
Cl(6)	1903 (2)	3546 (3)	1114 (4)	41 (3)
Cl(7)	3097 (4)	2500	2989 (6)	39 (4)
Cl(8)	3898 (3)	4516 (4)	-2333 (5)	59 (3)
P(1)	6283 (4)	2500	1336 (8)	45 (5)
P(2)	730 (4)	2500	-770 (7)	47 (5)
P(3)	3151 (3)	4596 (3)	2987 (5)	42 (3)
C(1)	6596 (19)	2041 (22)	2669 (32)	50 (10)
C(2)	6274 (21)	2500	3677 (37)	107 (14)
C(3)	6676 (18)	3531 (22)	1435 (31)	43 (9)
C(4)	7551 (29)	3622 (34)	1712 (47)	105 (19)
C(5)	6938 (23)	1991 (27)	481 (39)	74 (13)
C(6)	6943 (20)	2500	-692 (36)	100 (13)
C(7)	133 (14)	2500	425 (24)	54 (8)
C(8)	-820 (18)	2500	170 (30)	81 (11)
C(9)	358 (10)	3377 (13)	-1623 (17)	61 (5)
C(10)	377 (13)	4209 (16)	-1003 (21)	89 (8)
C(11)	3316 (11)	4259 (13)	4461 (18)	63 (6)
C(12)	4148 (12)	3942 (15)	4789 (21)	82 (7)
C(13)	2171 (11)	5051 (14)	3012 (19)	70 (6)
C(14)	1915 (13)	5574 (16)	1970 (22)	87 (8)
C(15)	3830 (10)	5473 (12)	2830 (17)	53 (5)
C(16)	3792 (12)	6184 (14)	3710 (20)	77 (7)
B(1)	1472 (11)	7475 (21)	4007 (17)	127 (20)
F(1)	1713 (19)	7551 (37)	2949 (19)	224 (11)
F(2)	789 (14)	7016 (25)	3984 (34)	224 (11)
F(3)	1333 (20)	8245 (24)	4430 (42)	224 (11)
F(4)	2053 (16)	7087 (30)	4666 (30)	224 (11)
Cl(9)	1664 (30)	2325 (50)	5700 (31)	148 (9)
Cl(10)	982 (25)	2888 (38)	3567 (16)	157 (10)
C(17)	856 (16)	2857 (28)	5013 (15)	117 (23)
Cl(11)	1318 (36)	4809 (31)	6018 (61)	313 (12)
Cl(12)	277 (15)	6072 (34)	6796 (77)	574 (22)
C(18)	1274 (12)	5734 (22)	6799 (40)	519 (63)

[a] All Ta and P atoms, and Cl(1)–Cl(8) were refined anisotropically.
[b] The refined occupancy was 0.46 (2) for the first CH_2Cl_2 molecule (Cl(9), Cl(10), and C(17)) and 0.96 (4) for the second CH_2Cl_2 (Cl(11), Cl(12), and C(18)).

We could not obtain the cis isomer of the niobium cluster complex. The ^{31}P NMR spectra of the niobium complexes always showed only one signal, which indicated they were trans. The X-ray structural determination confirmed the trans geometry of the tributylphosphine complex. During the chromatographic purification of the reaction products, we sometimes observed a small fraction, which was possibly the cis isomer.

Isomerization. To examine whether any trans–cis isomerization reaction would take place, we stirred a solution of **1** or **2** in ethanol, chloroform, acetone, or THF with or without triethylphosphine, lithium iodide, tetrabutylammonium chloride, silica gel, or activated charcoal for more than 4 h at room temperature or under reflux, and the products were examined with TLC (silica gel). Neither isomer was converted to the other under these conditions though partial decomposition occurred in some of the experiments. No isomerization took place also during the oxidation of the neutral complexes because the reduction of the oxidized species by tin dichloride yielded only the same isomer that had been used to make the oxidized species.

Structure. The results of X-ray structure determination are shown in Tables I–VII. The structures of the cluster units were drawn in Figures 1–4.

Like other hexanuclear cluster complexes of niobium and tantalum, all four complexes for which structures were determined in this study had octahedral metal clusters with 12 bridging chloro

Table V. Positional Parameters and (Equivalent) Isotropic Thermal Parameters[a] for *trans*-$[Nb_6Cl_{14}\{P(C_4H_9)_3\}_4]$[b]

atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	$U_{eq}/10^{-3}$ Å^2
Nb(1)	869.2 (5)	457.6 (4)	−742.3 (7)	45.9 (4)
Nb(2)	780.8 (5)	287.6 (4)	1597.4 (6)	45.4 (4)
Nb(3)	699.4 (5)	−837.2 (4)	66.2 (6)	44.6 (4)
Nb(1b)	5833.3 (5)	4490.6 (4)	−773.5 (6)	39.4 (4)
Nb(2b)	5653.5 (5)	4645.1 (4)	1547.8 (6)	40.1 (4)
Nb(3b)	5855.9 (5)	5780.5 (4)	324.7 (6)	40.6 (4)
Cl(1)	1921 (1)	867 (1)	1028 (2)	58 (1)
Cl(2)	1833 (2)	−458 (1)	−756 (2)	60 (1)
Cl(3)	81 (2)	181 (1)	−2739 (2)	57 (1)
Cl(4)	168 (2)	1510 (1)	−944 (2)	55 (1)
Cl(5)	1752 (1)	−641 (1)	1953 (2)	57 (1)
Cl(6)	99 (2)	1327 (1)	1803 (2)	56 (1)
Cl(7)	1890 (2)	1023 (1)	−1632 (2)	68 (1)
Cl(1b)	6729 (1)	3991 (1)	937 (2)	51 (1)
Cl(2b)	6973 (1)	5331 (1)	−497 (2)	51 (1)
Cl(3b)	5198 (1)	4841 (1)	−2715 (2)	53 (1)
Cl(4b)	4952 (1)	3502 (1)	−1280 (2)	55 (1)
Cl(5b)	6773 (1)	5501 (1)	2213 (2)	54 (1)
Cl(6b)	4772 (1)	3656 (1)	1429 (2)	53 (1)
Cl(7b)	6806 (2)	3869 (1)	−1719 (2)	59 (1)
P(1)	1820 (2)	643 (1)	3740 (2)	64 (2)
P(2)	1565 (2)	−1979 (1)	117 (2)	66 (2)
P(1b)	6515 (2)	4214 (1)	3631 (2)	60 (1)
P(2b)	7020 (2)	6804 (1)	775 (3)	76 (2)
C(1)	1444 (7)	1313 (5)	4486 (8)	79 (3)
C(2)	607 (7)	1173 (5)	4796 (9)	85 (3)
C(3)	269 (11)	1809 (8)	5218 (13)	154 (6)
C(4)	−547 (15)	1699 (10)	5373 (17)	228 (9)
C(5)	2013 (6)	5 (5)	4764 (8)	69 (3)
C(6)	2645 (7)	179 (5)	5941 (9)	82 (3)
C(7)	2790 (8)	−386 (6)	6697 (10)	93 (4)
C(8)	3498 (8)	−206 (6)	7820 (10)	108 (4)
C(9)	2930 (7)	945 (5)	3838 (9)	82 (3)
C(10)	3542 (9)	434 (6)	3539 (10)	108 (4)
C(11)	4566 (16)	702 (12)	3772 (21)	218 (10)
C(12)	4482 (28)	1001 (20)	3103 (33)	446 (27)
C(13)	790 (6)	−2662 (5)	−322 (8)	68 (3)
C(14)	1183 (7)	−3334 (5)	−299 (8)	76 (3)
C(15)	465 (7)	−3842 (6)	−662 (9)	89 (3)
C(16)	849 (8)	−4516 (6)	−659 (9)	98 (4)
C(17)	2356 (8)	−2167 (6)	1409 (11)	110 (4)
C(18)	1974 (10)	−2303 (7)	2256 (13)	138 (5)
C(19)	2630 (16)	−2367 (11)	3532 (21)	235 (10)
C(20)	3154 (17)	−1883 (13)	3983 (21)	272 (12)
C(21)	2157 (11)	−2084 (8)	−1096 (13)	142 (6)
C(22)	2905 (19)	−1960 (14)	−781 (25)	310 (15)
C(23)	3212 (15)	−2123 (10)	−2106 (18)	213 (9)
C(24)	4133 (24)	−1991 (17)	−1536 (30)	416 (20)
C(1b)	5971 (7)	3598 (5)	4214 (8)	72 (3)
C(2b)	5138 (7)	3784 (5)	4510 (8)	80 (3)
C(3b)	4792 (10)	3183 (7)	4946 (12)	129 (5)
C(4b)	4063 (14)	3306 (10)	5236 (17)	226 (9)
C(5b)	6785 (6)	4859 (5)	4746 (8)	68 (3)
C(6b)	7363 (7)	4670 (5)	5908 (9)	81 (3)
C(7b)	7637 (8)	5266 (6)	6682 (10)	99 (4)
C(8b)	8372 (10)	5140 (7)	7712 (12)	137 (5)
C(9b)	7566 (7)	3818 (5)	3742 (8)	75 (3)
C(10b)	8311 (8)	4248 (6)	3659 (9)	92 (4)
C(11b)	9157 (11)	3785 (8)	3818 (12)	141 (6)
C(12b)	9898 (15)	4216 (11)	3965 (18)	241 (10)
C(13b)	8145 (9)	6532 (7)	1589 (11)	119 (5)
C(14b)	8823 (16)	6959 (11)	1800 (19)	227 (10)
C(15b)	9763 (22)	6687 (15)	2630 (26)	277 (15)
C(16b)	9961 (21)	6231 (15)	2613 (27)	299 (17)
C(17b)	7194 (9)	7258 (7)	−347 (12)	128 (5)
C(18b)	7550 (10)	6935 (7)	−1106 (12)	133 (5)
C(19b)	7830 (10)	7412 (8)	−1979 (13)	146 (6)
C(20b)	8216 (11)	7085 (8)	−2741 (14)	160 (6)
C(21b)	6806 (11)	7473 (8)	1804 (14)	158 (6)
C(22b)	6146 (13)	7883 (10)	1259 (17)	204 (8)
C(23b)	5840 (16)	8243 (12)	2491 (20)	254 (11)
C(24b)	5194 (21)	8611 (16)	1695 (28)	381 (19)

[a] All carbon atoms were refined isotropically, and other atoms were refined anisotropically. [b] The atoms with the number followed by b are from cluster B and the others are from cluster A.

Table VI. Selected Bond Distances (Å) and Angles (deg) for *trans*-$[M_6Cl_{14}(PR_3)_4]^{n+}$[a]

	M = Ta, R = C_2H_5		M = Nb, R = C_4H_9 $n = 0$	
	$n = 0$	$n = 1$	cluster A	cluster B
M(1)–M(2)	2.908 (1)	2.946 (1)	2.960 (1)	2.956 (1)
M(1)–M(2)′	2.907 (1)	2.951 (1)	2.947 (1)	2.945 (1)
M(1)–M(3)	2.909 (1)	2.952 (1)	2.960 (1)	2.955 (1)
M(1)–M(3)′	2.907 (1)	2.952 (1)	2.949 (1)	2.953 (1)
M(2)–M(3)	2.887 (1)	2.915 (1)	2.925 (1)	2.929 (1)
M(2)–M(3)′	2.889 (1)	2.933 (1)	2.925 (1)	2.922 (1)
M(1)–M(1)′	4.140 (1)	4.208 (1)	4.218 (1)	4.213 (1)
M(2)–M(2)′	4.083 (1)	4.130 (1)	4.136 (1)	4.132 (1)
M(3)–M(3)′	4.085 (1)	4.141 (1)	4.137 (1)	4.142 (1)
M(1)–Cl(1)	2.466 (4)	2.447 (3)	2.458 (2)	2.462 (2)
M(1)–Cl(2)	2.464 (4)	2.446 (3)	2.460 (2)	2.462 (2)
M(1)–Cl(3)	2.457 (3)	2.447 (3)	2.464 (2)	2.462 (2)
M(1)–Cl(4)	2.459 (4)	2.448 (3)	2.458 (2)	2.447 (2)
M(2)–Cl(1)	2.457 (4)	2.447 (3)	2.456 (2)	2.455 (2)
M(2)–Cl(3)′	2.468 (3)	2.442 (3)	2.453 (2)	2.457 (2)
M(2)–Cl(5)	2.466 (4)	2.439 (3)	2.461 (2)	2.462 (2)
M(2)–Cl(6)	2.468 (3)	2.448 (3)	2.464 (2)	2.468 (2)
M(3)–Cl(2)	2.460 (4)	2.450 (3)	2.451 (2)	2.453 (2)
M(3)–Cl(4)′	2.454 (4)	2.443 (3)	2.452 (2)	2.450 (2)
M(3)–Cl(5)	2.465 (4)	2.440 (3)	2.464 (2)	2.466 (2)
M(3)–Cl(6)′	2.463 (3)	2.442 (3)	2.465 (2)	2.461 (2)
M(1)–Cl(7)	2.531 (4)	2.494 (3)	2.519 (3)	2.518 (2)
M(2)–P(1)	2.740 (4)	2.721 (3)	2.755 (3)	2.737 (3)
M(3)–P(2)	2.736 (4)	2.727 (3)	2.753 (3)	2.756 (3)
M(1)–Cl(1)–M(2)	72.40 (10)	74.02 (8)	74.09 (7)	73.90 (7)
M(1)–Cl(2)–M(3)	72.43 (10)	74.17 (7)	74.12 (7)	73.92 (7)
M(1)–Cl(3)–M(2)′	72.36 (10)	74.27 (8)	73.66 (7)	73.58 (7)
M(1)–Cl(4)–M(3)′	72.55 (10)	74.24 (8)	73.81 (7)	74.17 (7)
M(2)–Cl(5)–M(3)	71.68 (10)	73.38 (8)	72.86 (7)	72.92 (7)
M(2)–Cl(6)–M(3)′	71.71 (9)	73.71 (7)	72.79 (7)	72.73 (7)

[a] The atoms marked with a prime are related to those at *x*, *y*, *z* by the inversion center at the center of the cluster.

Table VII. Selected Bond Distances (Å) and Angles (deg) for *cis*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4][BF_4]\cdot 3CH_2Cl_2$

Ta(1)–Ta(1)′	2.962 (1)	Ta(2)–Cl(2)	2.440 (5)
Ta(1)–Ta(2)	2.941 (1)	Ta(2)–Cl(5)	2.438 (4)
Ta(1)–Ta(3)	2.941 (1)	Ta(3)–Cl(3)	2.433 (5)
Ta(1)–Ta(4)	2.950 (1)	Ta(3)–Cl(6)	2.454 (5)
Ta(2)–Ta(4)	2.927 (1)	Ta(4)–Cl(4)	2.430 (5)
Ta(3)–Ta(4)	2.933 (1)	Ta(4)–Cl(5)	2.436 (4)
Ta(4)–Ta(4)′	2.930 (1)	Ta(4)–Cl(6)	2.441 (5)
Ta(1)–Ta(4)′	4.169 (1)	Ta(4)–Cl(7)	2.441 (5)
Ta(2)–Ta(3)	4.132 (1)	Ta(1)–Cl(8)	2.482 (6)
Ta(1)–Cl(1)	2.438 (6)	Ta(2)–P(1)	2.707 (6)
Ta(1)–Cl(2)	2.441 (5)	Ta(3)–P(2)	2.709 (7)
Ta(1)–Cl(3)	2.444 (5)	Ta(4)–P(3)	2.718 (5)
Ta(1)–Cl(4)	2.456 (5)		
Ta(1)–Cl(1)–Ta(1)′	74.81 (18)	Ta(2)–Cl(5)–Ta(4)	73.80 (13)
Ta(1)–Cl(2)–Ta(2)	74.09 (14)	Ta(3)–Cl(6)–Ta(4)	73.62 (13)
Ta(1)–Cl(3)–Ta(3)	74.17 (14)	Ta(4)–Cl(7)–Ta(4)′	73.78 (15)
Ta(1)–Cl(4)–Ta(4)	74.29 (14)		

[a] The atoms marked with a prime are related to those at *x*, *y*, *z* by the mirror plane at *x*, $^1/_4$, *z*.

ligands on the edges. The six terminal positions on the apices were occupied by four trialkylphosphines and two chloro ligands. The average Ta–Ta distance was elongated on oxidation (2.901 Å in **1a** vs 2.942 Å in **10a** and 2.940 Å in **11a**). The average Ta–Cl(bridging) distance in the oxidized cluster (2.445 Å in **10a** and 2.441 Å in **11a**) was a little shorter than that in the neutral cluster (2.462 Å) while the Ta–Cl(terminal) distance showed a larger contraction on oxidation (2.531 Å in **1a** vs 2.494 Å in **10a** and 2.482 Å in **11a**). The average Ta–P distance was also shorter in the oxidized cluster (2.724 Å in **10a** and 2.710 Å in **11a**) than in the neutral cluster (2.738 Å). The average metal–metal distances of the neutral niobium cluster (2.944 Å) were longer than that of the corresponding tantalum cluster by 0.04 Å. However, the differences of the average metal–Cl and metal–P distances

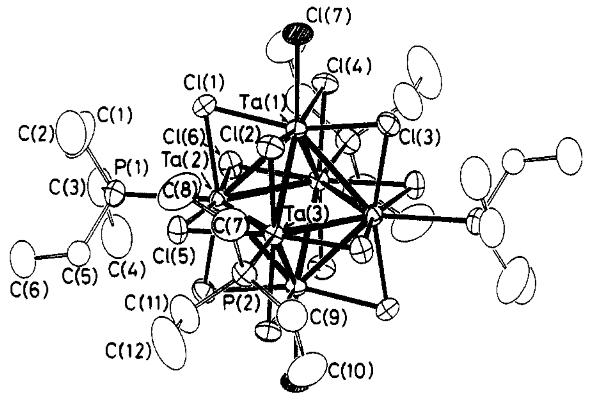

Figure 1. ORTEP drawing of *trans*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]$. All hydrogen atoms are omitted for clarity. The complex has a crystallographic inversion center at the center of the tantalum octahedron.

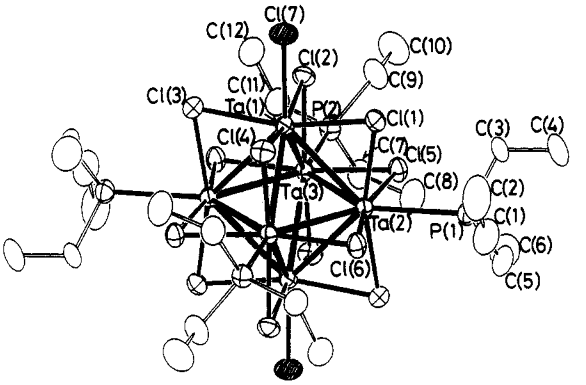

Figure 2. ORTEP drawing of the *trans*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]^+$ ion. The complex has a crystallographic inversion center at the center of the tantalum octahedron.

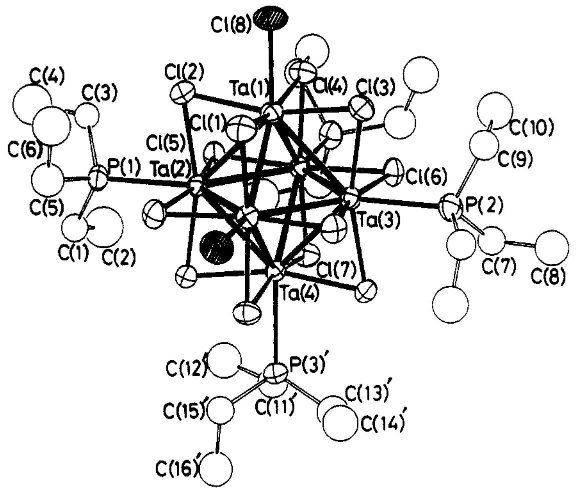

Figure 3. ORTEP drawing of the *cis*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]^+$ ion. The complex has a crystallographic mirror plane that passes through C(6), C(2), P(1), Ta(2), Cl(1), Cl(7), Ta(3), P(2), C(7), C(8), and the center of the tantalum octahedron. Only one of the disorder positions of C(1) and C(3)–C(5) were shown for clarity.

between the niobium and tantalum complexes were trivial (M–Cl(bridging) = 2.459 Å (Nb) vs 2.445 Å (Ta); M–Cl(terminal) = 2.519 Å (Nb) vs 2.531 Å (Ta); M–P = 2.750 Å (Nb) vs 2.738 Å (Ta)). The B–F distance of the tetrahedral tetrafluoroborate anion in **10a** was 1.37 Å on average.

Discussion

Isomerization. As described under Results, no isomerization reaction between cis and trans isomers has been observed. In mononuclear complexes, addition of a ligand or elimination of a coordinating ligand easily leads to the trans–cis isomerization. However, in the case of the cluster complexes, the elimination of a terminal ligand does not directly lead to the isomerization because the neighboring terminal ligand cannot move to the evacuated site due to the occupation of the bridging position by the bridging chloro ligands. Binding of a second ligand at one of the terminal position does not cause isomerization for the same reason.

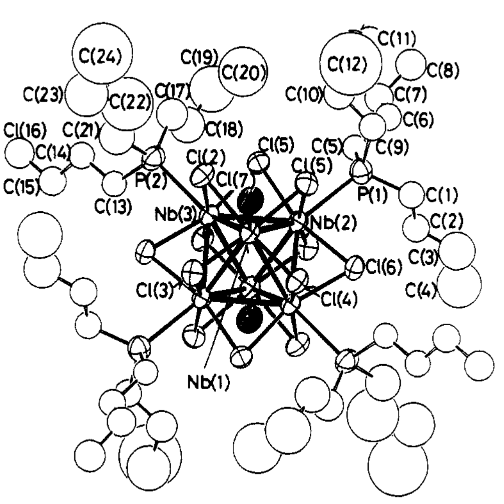

Figure 4. ORTEP drawing of *trans*-$[Nb_6Cl_{14}\{P(C_4H_9)_3\}_4]^+$. Of the two independent molecules in the structure, cluster A is shown here. The complex has a crystallographic inversion center at the center of the niobium octahedron.

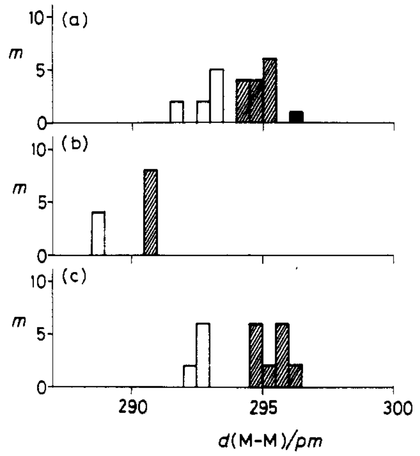

Figure 5. Histograms showing the distribution of metal–metal bond distances in the octahedral metal clusters. The ordinate *m* refers to the number of bonds in each range of 0.005 Å width, like 2.90–2.905 Å. The white rectangles correspond to the metal–metal bonds with phosphine ligands at both ends, the black rectangles to the bonds with chloro ligands at both ends, and the hatched rectangles to the bonds with a phosphine ligand and a chloro ligand. Key: (a) *trans*- and *cis*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]^+$; (b) *trans*-$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]$; (c) $[Nb_6Cl_{14}\{P(C_4H_9)_3\}_4]$.

Because no isomerization was observed under various conditions, it is very improbable that conversion of the geometry occurs in the reaction of the starting hydrate complex, $[Ta_6Cl_{14}(H_2O)_4]\cdot 4H_2O$, with the trialkylphosphine. Therefore, the starting hydrate complex in ethanol solution should contain both cis and trans isomers. The reported structural determination of the hydrate cluster indicated the trans geometry though the result did not look conclusive due to the disorder of the structure.[13] Our attempts to separate the isomers of the hydrate cluster complexes by chromatography were not successful.

Structure. From Figure 5, we can see the effect of the oxidation state of the cluster on the metal–metal bond distance. The trans and cis cationic complexes of tantalum (15 electrons) have longer average metal–metal bond distances than the neutral (16 electrons) by 0.039 Å. The tendency of the longer metal–metal bond distance

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[13] Burbank, R. D. *Inorg. Chem.* **1966**, *5*, 1491.

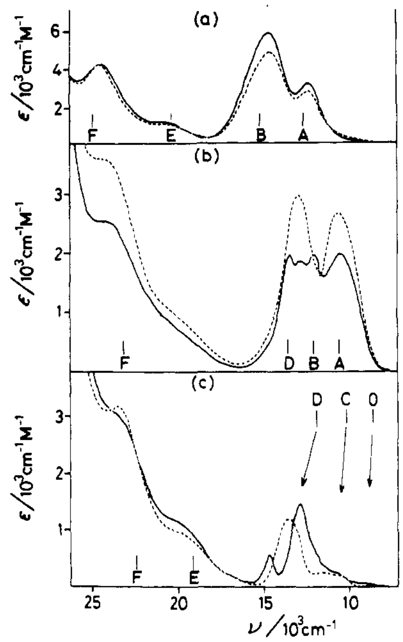

Figure 6. Electronic absorption spectra of (a) $[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]$ in CH_2Cl_2, (b) $[Ta_6Cl_{14}\{P(C_2H_5)_3\}][BF_4]$ in CH_2Cl_2, and (c) $[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4][BF_4]_2$ in CH_3CN. The spectra of the trans isomers are drawn with solid lines, and those of the cis isomer are drawn with broken lines. The spectra of *trans-* and *cis-*$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4][BF_4]_2$ were measured in the presence of $NOBF_4$ to prevent the reduction of the cluster. The small vertical lines indicate the position of absorption maxima of $[Ta_6Cl_{14}]^{2+}$ in DMSO (a), $[Ta_6Cl_{12}]^{3+}$ in ethanol (b), and $[Ta_6Cl_{18}]^{2-}$ in acetone (c) with the notations for the bands by Fleming and McCarley.[3] The small gaps of the spectra at 11.7×10^3 cm^{-1} are due to the switch of the detector.

in the higher oxidation state has already been observed and discussed in a series of niobium complexes, $[(Nb_6Cl_{12})Cl_6]^{n-}$ (n = 4, 3, 2).[14-18]

Figure 5 shows also the effect of the terminal ligand on the metal–metal bond distance; i.e., the bond distance between the metals depends on the kinds of ligands that are connected to these metals. The terminal chloro ligand makes the metal–metal bond longer than the phosphine ligand. Here, we will call this effect as "terminal ligand effect". One possible cause of this terminal ligand effect is the uneven distribution of the electronic charge among the metal atoms. It is probable that the metal atom connected with an anionic ligand has slightly more positive charge due to the neighboring negative charge than that connected with a neutral ligand. The electrostatic repulsion between neighboring metal atoms, each with partial positive charge, may lead to the longer metal–metal bonds of the metal bonded with an anionic ligand. Burbank attributed the large tetragonal distortion of the hydrate complex $[(Ta_6Cl_{12})Cl_2(H_2O)_4]$ to the oxidation states of four tantalum atoms close to +2, with the other two close to +3.[13] However, in the phosphine complexes studied here, the observed distortions are much smaller, and the difference of the charges on the metals cannot be so large as insisted for the hydrate complex. The ESR spectrum of $[Nb_6Cl_{14}\{P(C_3H_7)_3\}_4]$ reported by Klendworth and Walton shows that the unpaired electron locates on each metal with the same probability.[2]

Another possible cause of the terminal ligand effect is the "local matrix effect". The matrix effect in the cluster compounds has been discussed in detail by Corbett.[19] The existence of the matrix effect in the niobium and tantalum cluster complexes is evident when the average metal–metal bond distance of the chloro complex $K_4[Nb_6Cl_{18}]$ (2.915 Å)[20] is compared with that of the isomorphous bromo complex (2.971 Å).[21] The terminal ligands cannot approach the metal octahedron freely due to the van der Waals contact with the bridging ligands. If the most stable bond distance between the terminal ligand and the metal is shorter than the distance allowed by this van der Waals contact, the terminal ligand will draw the metal atom outward, and the metal–metal bond will be elongated. While the van der Waals radii of chlorine and of the phosphorus are approximately equal,[22] the metal–chloro bond distance is shorter than the metal–phosphine bond distance. As a result, chloro terminal ligands exert a larger "matrix effect" and elongate the metal–metal distances more than phosphine ligands.

The average Ta–Ta bond distance in $[(Ta_6Cl_{12})(H_2O)_6]^{3+}$ is reported to be 2.906 Å,[23] which is much smaller than those in the isomers of $[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]^+$ (2.942 Å for trans and 2.940 Å for cis). The shorter metal–metal bond lengths in the hydrate complex may be reasonable because the small aqua ligands exert a smaller matrix effect than the chloro and the phosphine ligands. On the other hand, the matrix effect does not explain why the average Nb–Nb bond distance in $[Nb_6Cl_{14}\{P(C_2H_5)_3\}_4]$ (2.944 Å) is longer than that in the $[Nb_6Cl_{18}]^{4-}$ complexes (2.915 Å in the K_4 salt[20] and 2.918 Å in the KGd salt[15]). The reason may be as follows. Because the anionic ligands donate more electron density to the metal cluster than the neutral ligands, the metal cluster with six terminal chloro ligands may contain more electron density for the metal–metal bonding[24] and have stronger metal–metal bonds than the cluster with two terminal chloro ligands.

Electronic Spectra. There has been no agreement yet about the assignments of the electronic absorption bands of the niobium and tantalum clusters though the subject has been discussed for a long time.[3-6] The first step in making the assignments is to correlate each absorption band of the oxidized clusters (15 and 14 electrons) with that of the 16-electron species. However, the correlations so far proposed have some ambiguity, for the intensity of the absorption band of these clusters changes so sensitively on oxidation or substitution of metal atoms that it is not very useful as a guide for such a correlation.[4]

The magnetic studies have established that the HOMO (highest occupied molecular orbital) in the 16-electron species is a nondegenerate state.[25,26] The molecular orbital calculations have shown that the HOMO is either a_{1g} or a_{2u}.[5,27,28] We will call this orbital HOMO[16] though it becomes the lowest unoccupied orbital in the 14-electron clusters.

Fleming and McCarley have correlated the absorption bands of many niobium and tantalum clusters mainly on the ground of their widths, and named them "A" to "M" bands.[3] According to their assignments, the "D" band, which is observed around 13.6 × 10³ cm⁻¹ in $[Ta_6Cl_{14}(C_2H_5OH)_6]^{3+}$ (15 electrons) and 11.85 × 10³ cm⁻¹ in $[Ta_6Cl_{18}]^{2-}$ (14 electrons), does not appear in the 16-electron cluster and is due to the transition to the HOMO[16]. On the other hand, Robbins and Thomson argued that the "B" band in the 16-electron cluster splits into the "B" and "D" band in the 15-electron cluster due to the spin-orbit coupling.[6]

The spectra of *trans-* and *cis-*$[Ta_6Cl_{14}\{P(C_2H_5)_3\}_4]^+$ (15 electrons) have distinct differences in the region around 13 × 10³ cm⁻¹

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(24) This does not mean that the metal atoms connected to the anionic ligands have more electron density than those bonded to the neutral ligands in the same cluster. What we discuss here is the total amount of the electron density donated to the metal cluster and not the distribution of the electronic density in the cluster, which may be related to the distortion of the cluster.

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(Figure 6B). The comparison of the spectrum of the trans complex with that of $[Ta_6Cl_{12}(C_2H_5OH)_6]^{3+}$ having the complete O_h symmetry reveals that the "D" band of the trans isomer splits into two bands. The comparison of the spectrum of the dicationic trans complex (14 electrons) with that of $[Ta_6Cl_{18}]^{2-}$ also leads to the same conclusion (Figure 6c). The splittings observed in the "D" bands of the oxidized trans isomers means that the "D" band corresponds to a transition from or to the degenerate state that splits into two levels in the trans isomer. If any band in the trans isomer with 16 electrons corresponds to this transition, it would also split into two as observed in the oxidized trans clusters. However, the spectra of the 16-electron clusters *trans*-$[Ta_6Cl_{14}(PR_3)_4]$ are almost identical with the spectrum of $[Ta_6Cl_{12}(DMSO)_6]^{2+}$ (Figure 6a). Therefore, the electronic spectra of the 16-electron clusters lack the "D" band as discussed by Fleming and McCarley, and this band must be assigned as a transition to the HOMO[16], $t_{2g} \rightarrow a_{2u}$ or $t_{1u} \rightarrow a_{1g}$.[3] Present results are not consistent with Robbins and Thomson's assignment.[6]

We will now discuss the difference in the "D" band between the trans and the cis oxidized clusters. Though the "D" band in the cis dicationic complex does not have distinct two peaks, the width of the band is larger than the width of each peak of the "D" band of the trans isomer (Figure 6c), and the "D" band of the cis isomer seems to have two overlapping peaks. In the spectrum of the cis monocationic complex (Figure 6b), the "D" band is overlapped with the "B" band, and we cannot see whether the band is made of only one component. Therefore, the difference in the "D" band between the trans and the cis isomers may be due to the degree of the splitting; i.e., the splitting of the trans isomer is much larger than that of the cis isomer.

We will take a hypothetical cluster having six terminal phosphine ligands with the complete O_h symmetry as the starting complex. The replacement of a phosphine ligand with a chloro ligand will perturb the molecular orbitals of the metal cluster. We will consider the effect of this perturbation on the three basal orbitals[29] of $t_{2g}(d_{xz},d_{yz})$ in the zeroth-order approximation.[30] If one of the phosphine ligands is replaced by a chloro ligand, the energies of the d_{xz} and the d_{yz} orbital on which the replacement takes place will be changed by ΔE, which can be positive or negative. If two phosphine ligands bonded to metals 3 and 6 (the trans positions) are replaced by chloro ligands, the energies of $\varphi_A = k(-d_{xz}(2) - d_{yz}(3) + d_{xz}(5) + d_{yz}(6))$ (Figure 7a) and $\varphi_B = k(-d_{yz}(1) - d_{xz}(3) + d_{yz}(4) + d_{xz}(6))$ (Figure 7b) will be changed approximately by 2Δ ($\Delta = k^2\Delta E$) because two of the four metal atoms constituting each basis orbital are bonded to the ligand to be replaced (in Figure 7d).[31] On the other hand, the energy of the basal orbital $\varphi_C = k(d_{xz}(1) - d_{yz}(2) - d_{xz}(4) + d_{yz}(5))$ (Figure 7c) will not be affected because no metal atom is bonded to the ligand to be replaced. Therefore, the splitting of the energy of the $t_{2g}(d_{xz},d_{yz})$ level is estimated to be 2Δ in the trans isomer (Figure 7e). On the other hand, if two phosphine ligands bonded to metals 3 and 1 (the cis positions) are replaced by chloro ligands, the energy of the basis orbital φ_A and φ_B will be changed by Δ, and φ_C by 2Δ as shown in Figure 7e. Therefore, the splitting of the $t_{1u}(d_{xz},d_{yz})$ orbital in the trans isomer must be twice as large as that in the cis isomer. Similar discussion with the orbitals $t_{2g}(d_{xz},d_{yz})$, $t_{1u}(d_{z^2})$, $t_{2g}(d_{xy})$, and $t_{1u}(d_{xz},d_{yz})$ leads to the same conclusion, and the splitting of the "D" band in the trans isomer should be twice as large as that in the cis isomer whether the transition is $t_{2g} \rightarrow a_{2u}$ or $t_{1u} \rightarrow a_{1g}$.

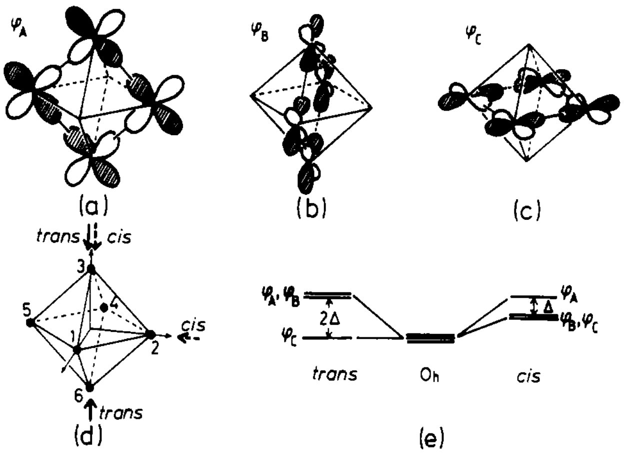

Figure 7. (a–c) Basal orbitals of $t_{2g}(d_{xz},d_{yz})$: (a) $\varphi_A = k(-d_{xz}(2) - d_{yz}(3) + d_{xz}(5) + d_{yz}(6))$, (b) $\varphi_B = k(-d_{yz}(1) - d_{xz}(3) + d_{yz}(4) + d_{xz}(6))$, and (c) $\varphi_C = k(d_{xz}(1) - d_{yz}(2) - d_{xz}(4) + d_{yz}(5))$. (d) Numbering scheme of the metal atoms and the positions where the replacement takes place in the trans and cis isomer. (e) Splitting of the $t_{2g}(d_{xz},d_{yz})$ orbital in the trans and cis isomers.

Conclusions

Both trans and cis isomers of the tantalum cluster complexes $[Ta_6Cl_{14}(PR_3)_4]^{n+}$ (R = alkyl, n = 0–2) can be isolated, and they are not easily converted to each other. The trans and cis geometries of the terminal ligands influence not only the physical properties like solubility in the organic solvents but also the structure and the electronic states of the metal cluster. The structural influence can be summarized as follows: the terminal chloro ligand makes the metal–metal bond distances involving the metal connected with it shorter than the phosphine ligand. This effect is on the order of 0.02 Å and is observed also in the niobium complex. The influence of the geometry on the electronic states of the metal cluster was obvious in the splitting of the absorption band at around 13×10^3 cm^{-1} of the oxidized species. The splitting was much larger in the trans isomer than in the cis, which can be explained by a simple zeroth-order approximation scheme.

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Supplementary Material Available: Tables giving details of the crystallographic X-ray data collection, thermal parameters, positional parameters of hydrogen atoms, and detailed lists of bond distances and angles (21 pages); listings of observed and calculated structure factors (70 pages). Ordering information is given on any current masthead page.

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(29) For the details and the notations of the molecular orbitals of niobium and tantalum clusters, see refs 6 and 26.

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(31) We assume that the terminal ligand interacts only with the atomic orbitals of the metal atom with which it is bonded. Therefore, the cross terms like $\langle d_{yz}(3)|H_1|d_{xz}(2)\rangle$, where H_1 is the Hamiltonian of the perturbation, are always zero.