meaningful to discuss them briefly. The $SrCl_2$ structure is of the familiar fluorite type: each Sr atom is located in a body-centered-cubic environment of Cl atoms, and each Cl atom is in a tetrahedral configuration of Sr atoms. The structure of SrI_2 is in many respects quite different, since the Sr atom is sevenfold coordinated by iodine atoms located in essentially two planes on either side of the Sr atom. Four of the iodine atoms form a slightly deformed square with the remaining three atoms describing a triangle. The two I atoms in SrI_2 are structurally different. One iodine atom is coordinated to three Sr atoms in the form of a triangular face; the other is tetrahedrally coordinated by four Sr atoms, reminiscent of the coordination polyhedron about the anion in $SrCl_2$.

The sevenfold Br atom coordination of the Sr(1) atom is comparable to that observed for Sr atoms in the SrI_2 structure. The Br(1) and Br(2) atoms are found trigonally and tetrahedrally coordinated to metal atoms, respectively, as are the two I atoms in SrI_2. However, the coordination polyhedra around the Sr(1), Br(1), and Br(2) atoms are not quite as regular as are their counterparts in the SrI_2 structure.

The presence of tetrahedrally coordinated Br atoms, namely, Br(2), Br(3), and Br(4), and an eightfold coordinated metal atom, Sr(2), in $SrBr_2$ is indicative of the similarity of this structure to that of $SrCl_2$ although in $SrCl_2$ the coordination about the Sr atom is cubic while in $SrBr_2$ it is square antiprismatic. The existence of the sevenfold coordinated Sr atoms and the trigonally coordinated halide atom in both $SrBr_2$ and SrI_2 establishes the similarity between these two structures. Therefore, this $SrBr_2$ structure may be considered a hybrid which incorporates features of both the $SrCl_2$ and the SrI_2 structures.

In addition to the above-mentioned common structural characteristics of $SrBr_2$, $SrCl_2$, and SrI_2, a unique feature of this structure is the alternation of Sr atoms and vacancies along the chain of antiprisms. At 25°, the temperature at which the work was done, the two kinds of antiprisms, one containing an Sr(2) atom and one containing a void region, are clearly different. The antiprism containing the Sr(2) atom exhibits significantly shorter distances from the metal atom to the bromine atoms at the corners of the surrounding polyhedron, namely, 3.115 and 3.165 Å, than analogous distances for the empty antiprism with the vacancy hypothetically located halfway along the *c* axis from the Sr(2) atom, in this case, 3.181 and 3.333 Å. This difference is precisely what would be expected since Sr(2) is bonded to Br(1) and Br(2) while obviously the vacancy is not bonded to anything. However, at higher temperatures, it could be suggested that indeed the lattice would relax and allow partial occupancy of the Sr(2) atom in the two twofold positions with the two types of antiprism becoming structurally more similar to if, indeed, not identical with each other.

On the basis of certain similarities in powder photographs, earlier workers[1,3] have reported that $SrBr_2$, $SmBr_2$, and $EuBr_2$ are isostructural. In view of the considerable amount of controversy due in part to the insensitivity of the powder method to permit a determination of the occupancy parameter of one Sr atom in $SrBr_2$, we suggest that in $SmBr_2$ and $EuBr_2$ partial occupancy may well occur at 25°, to say nothing at all about the situation at higher temperatures. Only when single-crystal X-ray studies currently in progress have been completed can definitive statements be made about the isostructural character of these dibromides.[15]

Acknowledgment.—The support of the U. S. Atomic Energy Commission [Contract AT(11-1)-716] is acknowledged gratefully.

(15) H. Beck and H. Baerninghausen, private communication.

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The Crystal Structure of $H_2[Ta_6Cl_{18}] \cdot 6H_2O$[1]

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Received October 30, 1970

The structure of $H_2[Ta_6Cl_{18}] \cdot 6H_2O$ has been determined by three-dimensional single-crystal X-ray analysis. The compound crystallizes in the cubic space group $Fd3m(O_h^7)$ with a unit cell dimension at $23 \pm 3°$ of $a = 19.92$ (1) Å. The derived structure was refined by least-squares methods to a conventional R index of 5.3%. The unit cell is composed of eight distinct and regular octahedral $Ta_6Cl_{18}^{2-}$ anion clusters (O_h symmetry) with centers at ($^1/_8$, $^1/_8$, $^1/_8$), ($^1/_8$, $^5/_8$, $^5/_8$), ($^5/_8$, $^5/_8$, $^1/_8$), and ($^5/_8$, $^1/_8$, $^5/_8$), and the four others related to these by the center of symmetry. The Ta–Ta distance, uncorrected for thermal motion, is 2.962 (2) Å. The terminal Ta–Cl distance of 2.507 (9) Å is significantly longer than the bridging Ta–Cl distance of 2.414 (5) Å.

Introduction

A number of compounds have been reported of the type $(M_6X_{12})Y_mL_{6-m}^{(n-m)+}$ where M = Nb, Ta; X = halogen; Y = halogen; L = neutral electron-donating ligand such as H_2O; m = number of Y groups; and n = charge on the M_6X_{12} unit. Structural information on a number of $M_6X_{12}^{n+}$-containing compounds[2-7] has shown

(1) Research carried out at the Ames Laboratory of the U. S. Atomic Energy Commission. Ames Laboratory Contribution No. 2791.

(2) R. D. Burbank, *Inorg. Chem.*, **5**, 1491 (1966).

(3) D. Bauer, H. G. Schnering, and H. Schafer, *J. Less-Common Metals*, **8**, 388 (1965).

(4) D. Bauer and H. G. Schnering, *Z. Anorg. Allg. Chem.*, **361**, 259 (1968).

(5) V. A. Simon, H. G. Schnering, H. Wohrle, and H. Schafer, *ibid.*, **339**, 155 (1965).

(6) V. A. Simon, H. G. Schnering, and H. Schafer, *ibid.*, **361**, 235 (1968).

(7) H. Schafer, H. G. Schnering, K. J. Niehues, and H. G. Nieder-Vahrenholz, *J. Less-Common Metals*, **9**, 95 (1965).

that the complex ion $M_6X_{12}^{n+}$ with $n = 2$–4 appears as a structural principle in all polynuclear subhalides of this type, with the tendency to coordinate additional ligands in an octahedral pattern in the solid state. Burbank[2] has further concluded that although four negative ligands consistently coordinate to flatten the M_6 polynucleus, two negative ligands lead to elongation of the M_6 polynucleus, and six negative ligands give rise to an undistorted equilibrium symmetry.

Since the chemistry of polynuclear subhalides is still in its formative stage we felt that structural information of another $M_6X_{12}^{n+}$-containing compound would be of interest. Therefore we undertook an X-ray study of $H_2[Ta_6Cl_{18}]\cdot 6H_2O$ for which $n = 4$.

Experimental Section

A sample of the compound was kindly supplied by Dr. R. E. McCarley,[8] and dark red crystals were obtained by recrystallization from a hydrochloric acid solution through which chlorine gas had been passed. Microscopic examination revealed that the crystals were octahedral with sharply defined edges. Crystals were selected and mounted in thin-walled Lindemann glass capillaries to prevent decomposition in the atmosphere. Preliminary precession photographs exhibited $m3m$ symmetry indicating a cubic space group. The conditions limiting the possible reflections were hkl where $h + k = 2n\mathfrak{C}$, hhl when $l + h = 2n\mathfrak{C}$, $0kl$ when $k + l = 4n$, $(k, l = 2n)\mathfrak{C}$. These conditions are consistent with space group $Fd3m(O_h^7)$. The unit cell parameter at 23 ± 3° is $a = 19.92\ (1)$ Å, as determined by a least-squares fit to 13 independent reflection angles whose centers were determined by left–right, top–bottom beam splitting on a previously aligned General Electric XRD-5 counter diffractometer (Mo Kα radiation, λ 0.7107 Å). The unit cell was assumed to contain eight molecules of $H_2Ta_6Cl_{18}\cdot 6H_2O$ leading to a calculated density of 3.08 g/cm^3; the density was difficult to measure because of the porosity of the crystal.

For data collection, a crystal having approximate dimensions 0.10 × 0.10 × 0.086 mm along the a, b, c crystal axes, respectively, was mounted such that the 0.086-mm axis was along the spindle axis.

Data were collected at room temperature (23 ± 3°) with a General Electric XRD-5 diffractometer equipped with a scintillation counter and using zirconium-filtered molybdenum Kα radiation (λ 0.7107 Å). Within a 2θ sphere of 50°, all data in one-sixth of an octant ($h \geq k \geq l$) were recorded using the θ–2θ scan technique with a takeoff angle of 3°. A symmetric scan range of 3.33° in 2θ was used and stationary-crystal, stationary-counter background counts were made at each end of the scan. Counting times for the latter were 20 sec if $2\theta \geq 15°$ and 40 sec if $2\theta < 15°$. The scan rate was 2°/min. A total of 365 reflections were measured in this way.

As a general check on electronic and crystal stability, the intensities of three standard reflections (642, 911, and 800) were remeasured periodically during the data collection period. These reflections decreased slowly in intensity, the decrease being about 6.5% during the entire period of data collection; such a decrease was considered quite acceptable and the data were appropriately corrected.

The intensity data were also corrected for Lorentz–polarization effects and for effects due to absorption. The absorption coefficient, μ, is 194.49 cm^{-1}, and an absorption correction was made using a computer program by Wehe, *et al.*[9] The maximum and minimum transmission factors were 26.6 and 29.4%, respectively. Of the 365 measured intensities, 214 were found to be above background (*i.e.*, greater than 3 times the standard error based on counting statistics) and therefore considered as observed. The unobserved reflections were not used in the solution and refinement of the derived structure.

The estimated error in each intensity measurement was calculated by $[\sigma(I_o)]^2 = [C_t + J*C_b + (K_t*C_t)^2 + (K_b*J*C_b)^2 + (K_a*C_r)^2]/(A*Lp)^2$ where J is $^5/_2$ or $^5/_4$ depending on whether background counts were measured for 20 or 40 sec, respectively, and where C_t and C_b are the total count and the background count, respectively. Also $C_r = C_t - J*C_b$, A is the transmission factor, and K_t, K_b, and K_a are the fractional random errors in C_t, C_f, and A, respectively. A value of 0.04 was arbitrarily assigned to K_t, K_b, and K_a since our previous studies have shown this to produce reliable weights. The estimated standard deviation in each structure factor was calculated by

$$\sigma(F_o) = [(I_o) + \sigma(I_o)]^{1/2} - |F_o|$$

a function based on the finite difference method.[10] These standard deviations were used during the least-squares refinements to weight the observed structure factors where w, the individual weighting factor, was defined as $1/\sigma(F_o)$.[2]

Solution and Refinement of the Structure.—Examination of the Patterson function readily revealed trial positions for the tantalum cluster. The positions were then refined by full-matrix least-squares methods with isotropic thermal parameters to a conventional discrepancy factor of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.135$ and a weighted R factor of $R_w = (\Sigma w(|F_o| - |F_c|)^2)^{1/2} = 0.143$. The scattering factors used were those of Cromer and Waber[11] with modifications for the real and imaginary parts of anomalous dispersion.[12]

A difference electron density map[13] at this stage showed that apparently all atoms had been accounted for but that some anisotropic motion, particularly of the heavier atoms, was quite evident.

After adding the ten anisotropic thermal parameters allowed by symmetry,[14] there were a total of 15 parameters to be varied and therefore, 13 reflections/variable. Therefore a full-matrix anisotropic least-squares refinement was considered justified.

Final values of R and R_w of 0.053 and 0.055, respectively, were obtained. Even though no oxygen atoms had been added to the refinement, a final difference electron density map was calculated and exhibited no peak above 1 e$^-$/Å^3 in any chemically reasonable position. Therefore, the water molecules were assumed to be disordered.

In Table I are given the final values of the positional parameters, along with their standard deviations as derived from the inverse matrix of the last cycle of the least-squares refinement. In Table II are given the values of F_o and F_c in electrons for the 214 reflections above background. The values of F_c for unobserved reflections in no case exceeded $3\sigma(F_o)$. An indication of the directions and root-mean-square amplitudes of vibration for the atoms refined anisotropically is provided by Table III.

TABLE I

FINAL POSITIONAL PARAMETERS FOR $H_2[Ta_6Cl_{18}]\cdot 6H_2O$[a]

Atom	Position	X/a	Y/b	Z/c
Ta	48f	0.23016 (7)	0.125	0.125
Cl(term)	48f	0.35606 (46)	0.125	0.125
Cl(bridge)	96g	0.12543 (47)	Z/c	0.24526 (22)

[a] Numbers in parentheses represent standard deviations occurring in the last digit of the parameter. Origin is at center of symmetry.

Description and Discussion

The unit cell of crystalline $H_2[Ta_6Cl_{18}]\cdot 6H_2O$ showing only the $Ta_6Cl_{18}^{2-}$ anions is illustrated[15] in Figure 1. The tantalum and terminal chlorine atoms lie in positions of mm crystallographic symmetry, while the bridging chlorines lie on mirror planes. The effect is to give a cell consisting of eight distinct and regular octahedral $Ta_6Cl_{18}^{2-}$ anion clusters (O_h symmetry), with

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(8) B. G. Hughes, J. L. Meyer, P. B. Fleming, and R. E. McCarley, *Inorg. Chem.*, **9**, 1343 (1970).

(9) D. J. Wehe, W. R. Busing, and H. A. Levy, "A Fortran Program for Single-Crystal Orienter Absorption Corrections," Report ORNL-TM-299, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(10) D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

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

(12) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(13) M. L. Hackert, computer program, private communication, Ames, Iowa 1968.

(14) H. A. Levy, *Acta Crystallogr.*, **9**, 679 (1956).

(15) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for the Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

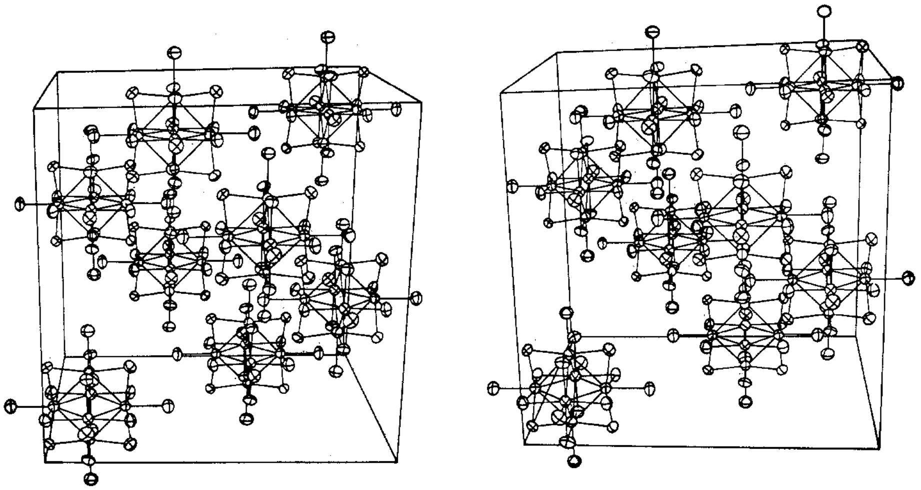

Figure 1.—A stereoscopic view of the packing of $Ta_6Cl_{18}^{2-}$ anion clusters in the unit cell. The view corresponds to a right-handed coordinate system with the origin in the front lower left corner with the *x* axis horizontal.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS) FOR $H_2[Ta_6Cl_{18}]\cdot 6H_2O$

	K	L	FO	FC
H = 1	1	1	2186	-2577
H = 2	2	0	1598	-1482
H = 3	1	1	839	-746
	3	1	249	-279
	3	3	969	-676
H = 4	0	0	1434	-1382
	2	2	688	-682
	4	0	712	-602
	4	4	650	871
H = 5	1	1	434	342
	3	1	535	-518
	3	3	841	805
	5	1	689	738
	5	3	1052	971
	5	5	1225	-1152
H = 6	2	0	319	349
	4	2	1265	1273
	6	0	392	505
	6	4	1792	-1758
H = 7	1	1	1248	1240
	3	3	708	785
	5	1	316	317
	5	3	949	-965
	5	5	1113	-1126
	7	1	343	389
	7	3	543	-547
	7	5	765	764
	7	7	327	212
H = 8	0	0	3409	3622
	2	2	669	-713
	4	0	450	-594
	4	4	958	-927
	6	6	761	742
	8	0	2346	2375
	8	8	1690	1583
H = 9	1	1	1861	-1960
	3	1	775	-748
	3	3	111	-44
	5	1	410	414
	5	3	288	-272
	5	5	492	478
	7	1	1079	1106
	7	3	219	-144
	7	5	43	108
	7	7	506	490
	9	1	1562	-1593
	9	3	769	-711
	9	5	475	442
	9	7	990	960
	9	9	1376	-1335
H = 10	2	0	1675	-1739
	4	2	147	100
	6	0	862	894
	6	4	418	431
	8	2	1097	-1098
	8	6	459	449
	10	0	1686	-1768
	10	4	481	475
	10	8	1269	-1230
H = 11	1	1	1011	-981
	3	1	268	287
	5	3	258	246
	5	5	314	388
	7	1	455	-409
	7	3	152	134
	7	5	315	-309
	9	1	881	-896
	9	3	329	318
	9	5	115	135
	9	7	456	-430
	9	9	827	-806
	11	1	516	521
	11	3	194	178
	11	5	110	-70
	11	7	242	-195
	11	9	479	472
	11	11	341	324
H = 12	0	0	1165	-1226
	2	2	82	66
	4	4	371	399
	6	2	430	404
	6	6	795	-790
	8	0	749	-731
	8	4	212	-266
	8	8	404	-382
	10	2	422	408
	10	6	62	-20
	10	10	636	581
	12	0	258	303
	12	4	88	63
	12	12	187	-164
H = 13	1	1	346	322
	3	1	127	-149
	3	3	360	351
	5	1	313	314
	5	3	510	508
	5	5	667	-650
	7	3	453	-454
	7	5	582	-579
	7	7	399	380
	9	1	344	334
	9	3	139	-69
	9	5	234	205
	9	7	116	-7
	9	9	333	343
	11	1	209	157
	11	3	71	28
	11	5	167	148
	11	7	138	-101
	11	9	188	163
	11	11	180	-160
	13	1	73	110
	13	3	265	262
	13	5	351	-363
	13	7	322	-297
	13	9	58	59
	13	11	142	43
	13	13	146	-194
H = 14	2	0	53	69
	4	2	834	795
	6	0	399	422
	6	4	1153	-1122
	8	2	169	-178
	8	6	563	567
	10	0	416	416
	10	4	364	322
	10	8	211	171
	12	2	315	290
	12	6	224	-544
	12	10	42	25
	14	0	305	362
	14	4	777	-778
	14	8	440	447
	14	12	384	-396
H = 15	1	1	308	308
	3	1	294	290
	3	3	695	681
	5	1	460	451
	5	3	828	-803
	5	5	925	-900
	7	3	581	-549
	7	5	673	686
	7	7	330	385
	9	1	319	356
	9	5	257	292
	9	9	364	349
	11	3	256	257
	11	5	391	-372
	13	3	450	-451
	13	5	529	-519
	13	7	393	403
	13	13	299	-296
	15	3	477	-492
	15	5	560	585
	15	7	406	403
H = 16	0	0	1192	1219
	4	0	184	191
	4	4	1015	-1022
	6	2	474	-494
	6	6	832	830
	8	0	806	801
	8	4	323	346
	8	8	520	497
	10	2	256	-254
	10	10	442	-436
	12	0	183	-88
	12	4	463	-494
	14	2	388	-401
	14	6	670	615
	16	0	162	203
	16	4	405	448
H = 17	1	1	780	-773
	3	3	258	-241
	5	3	315	-371
	5	5	470	486
	7	1	410	411
	7	5	241	243
	9	1	685	-674
	9	3	231	-226
	9	7	355	272
	9	9	669	-599
	11	1	313	-258
	11	9	372	-343
	13	5	253	273
	15	1	150	100
H = 18	2	0	910	-913
	6	0	488	490
	8	2	610	-606
	10	0	910	-950
	10	4	218	234
	10	8	682	-679
	14	0	197	234
H = 19	1	1	619	-646
	3	1	255	295
	7	1	317	-355
	9	1	580	-581
	9	3	268	276
	9	7	347	-335
	9	9	485	-521
	11	1	396	377
	11	9	355	329
H = 20	0	0	785	-822
	2	2	299	312
	8	0	553	-569
	8	8	380	-376
	10	2	419	412
	12	0	354	339
H = 21	1	1	340	309
H = 22	2	0	239	180
	6	0	210	51
	6	4	369	-351
H = 23	5	3	327	-335
H = 24	0	0	310	318

TABLE III

FINAL ANISOTROPIC THERMAL PARAMETERS ($\times 10^5$) FOR $H_2[Ta_6Cl_{18}]\cdot 6H_2O$[a,b]

	Position	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ta	48f	172 (5)	193 (3)	β_{22}	0.0	0.0	4 (5)
Cl(term)	48f	213 (26)	337 (20)	β_{22}	0.0	0.0	13 (35)
Cl(bridge)	96f	314 (20)	β_{33}	203 (9)	β_{13}	28 (14)	−29 (12)

[a] The form of the anisotropic temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses are standard deviations occurring in the last digit of the parameter.

centers at $({}^1/_8, {}^1/_8, {}^1/_8)$, $({}^1/_8, {}^5/_8, {}^5/_8)$, $({}^5/_8, {}^5/_8, {}^1/_8)$, and $({}^5/_8, {}^1/_8, {}^5/_8)$, and the four others related to these by the center of symmetry. Also there are "holes" (~9-Å diameter) in the structure with centers at $({}^3/_8, {}^3/_8, {}^3/_8)$, $({}^1/_8, {}^5/_8, {}^1/_8)$, $({}^5/_8, {}^1/_8, {}^1/_8)$, and $({}^1/_8, {}^1/_8, {}^5/_8)$, plus the four others related to these by the center of symmetry. This arrangement of tantalum clusters and "holes" is that of two interpenetrating diamond-type lattices, respectively. The $Ta_6Cl_{18}^{2-}$ ion cluster is stereoscopically shown in Figure 2.

Comparison of van der Waals contacts between clusters and intracluster distances is provided in Table IV. Bond lengths, both uncorrected for thermal motion and corrected using the riding model approximation, are given in Table V. The terminal Ta–Cl distance of 2.507 (9) Å is significantly longer than the bridging Ta–Cl distance of 2.414 (5) Å, and such a lengthening is in agreement with other polynuclear subhalides.[3-7] The Ta–Ta distance of 2.962 (2) Å as well as bridging and terminal Ta–Cl distances in the $Ta_6Cl_{18}^{2-}$ cluster compare favorably with the structural data about other $(M_6X_{12})Y_mL_{6-m}^{(n-m)+}$ species, as indicated in Table VI. A comparison of the results in this table shows that there is a consistent lengthening of the M–M distance upon oxidation of the $M_6X_{12}^{n+}$ cluster. The M–Y (terminal) distance is also shortened upon oxidation of the $M_6X_{12}^{n+}$ cluster and is shorter than one would expect after equilibration of the intracluster repulsion forces due to lengthening of the M–M distance. Our results appear reasonable in view

TABLE IV

VAN DER WAALS CONTACTS BETWEEN CLUSTERS AND INTRACLUSTER DISTANCES[a,b]

	Length Å	
Atoms	Between clusters	In same cluster
Cl(term)–Cl(bridge)	3.675 (0.006)	3.250 (0.008)
Cl(bridge)–Cl(bridge)	3.671 (0.013)	3.384 (0.017)
Cl(term)–Cl(term)	5.007 (0.003)	6.499 (0.017)

[a] Numbers in parentheses refer to the standard deviations. [b] All distances are uncorrected for thermal motion.

TABLE V

COMPARISON OF BOND LENGTHS USING THE RIDING MODEL CORRECTION FOR THERMAL MOTION[a,b]

	Length, Å	
Bond	Uncor	Riding motion
Ta–Cl(term)	2.507 (0.009)	2.519 (0.009)
Ta–Cl(bridge)	2.414 (0.005)	2.421 (0.005)
Ta–Ta	2.962 (0.002)	2.962 (0.002)

[a] Numbers given in parentheses refer to the standard deviations. [b] Second atom assumed to ride on the first.

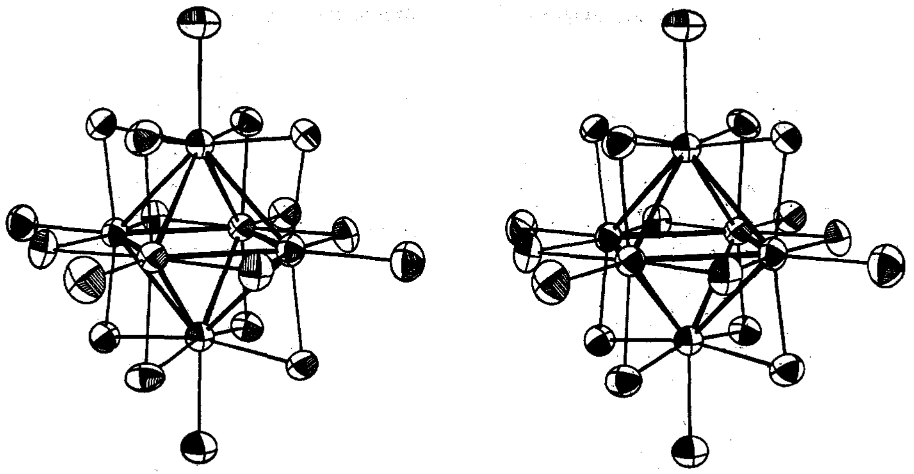

Figure 2.—A stereoscopic view of the $Ta_6Cl_{18}^{2-}$ anion cluster.

TABLE VI
COMPILATION OF SOME DISTANCES[a] IN $(M_6X_{12})Y_mL_{6-m}^{(n-m)+}$-CONTAINING COMPOUNDS

Compd	d(M–M), Å		d(M–X), Å	d(M–Y), Å	d(X–X), Å
Ta_6I_{14}[2]	2.805 3.080	2.90^b	2.754		3.785
$Ta_6Cl_{14}\cdot 7H_2O$[3]	2.96				
Ta_6Cl_{15}[4]	2.925		2.434	2.564	3.408
$H_2[Ta_6Cl_{18}]\cdot 6H_2O$	2.962		2.414	2.507	3.384
Nb_6Cl_{15}[5]	2.895 2.955	2.915^b	2.407	2.58	3.385
$K_4(Nb_6Cl_{18})$[6]	2.915		2.49	2.596	3.47
Nb_6F_{15}[7]	2.80		2.05	2.11	2.89
$[(CH_3)_4N]_2Nb_6Cl_{18}$[8]	3.02		2.42	2.46	3.40

[a] All distances refer to average values. [b] Tetragonal flattening.

of molecular orbital studies of the $M_6X_{12}^{n+}$ species.[16,17] Infrared spectra of these polynuclear subhalides with $n = 3$ or 4 have been interpreted on the basis of tighter binding in the M–Y(terminal) bond.[18]

It would be reasonable to assume that the six waters and two protons reside in the approximately 9-Å "holes" in the structure, but with no preferred ordering. This would account for the fact that there were no peaks found on the difference map above a value of 1 e⁻/Å³, although no oxygen atoms had been included in the structure factor calculation.

In $HNb_6I_8^{3+}$,[19] the hydrogen atom was found to reside in the center of the Nb_6 cluster, but chemical evidence[20] seems to rule out a similar position for the proton in this case.

(16) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).
(17) R. F. Schneider and R. A. Mackay, *J. Chem. Phys.*, **42**, 843 (1968).
(18) P. B. Fleming and R. E. McCarley, *Inorg. Chem.*, **9**, 1347 (1970).
(19) A. Simon, H. G. Schnering, and H. Schafer, *Z. Anorg. Allg. Chem.*, **355**, 311 (1967).
(20) R. E. McCarley, private communication.

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The Stereochemistry of the Chloropentaaquoterpyridylpraseodymium(III) Ion[1]

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Received January 26, 1970

The crystal structure of $Pr(C_{15}H_{11}N_3)Cl_3(H_2O)_8$ has been determined by single-crystal X-ray diffraction techniques employing Patterson and Fourier syntheses. The compound crystallizes in the space group *Cm* ($Z = 2$) with dimensions $a = 7.482$ (2), $b = 16.602$ (7), $c = 9.723$ (3) Å, and $\beta = 90.13$ (1)°. The structure was refined to a discrepancy factor of 0.022 for 2005 diffractometer data. The coordination sphere about the Pr(III) ion consists of three nitrogen atoms from the terpyridyl ligand, one chloride ion, and five oxygen atoms from water molecules in the form of a monocapped square-antiprismatic polyhedron.

Introduction

In recent years a large number of rare earth complexes with donor nitrogen atoms have been prepared using nonbasic nitrogen-containing ligands. Prominent among these are complexes of polypyridyl ligands which include $Ln(terpy)Cl_3(H_2O)_n$,[3,4] $Ln(terpy)(NO_3)_3(H_2O)_n$,[5] $Ln(bipy)_2(NO_3)_2(H_2O)_n$,[6,7] $Ln(bipy)_2Cl_3$-

(1) (a) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 17, 1969. (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (No. 841-G), and to the National Science Foundation (GP-15070).

(2) (a) National Defense Education Act Fellow, 1966–1969; Petroleum Research Fund Fellow, 1969–1970. (b) This article is based in part on a dissertation submitted by L. J. Radonovich to the Graduate School of Wayne State University in partial fulfillment of the requirements for the Ph.D. degree.

(3) S. P. Sinha, *Z. Naturforsch. A*, **20**, 552 (1965).

(4) Ln denotes the series of lanthanide(III) ions. Terpyridyl is denoted by terpy.

(5) S. P. Sinha, *Z. Naturforsch. A*, **20**, 1661 (1965).

(6) S. P. Sinha, *Spectrochim. Acta*, **20**, 879 (1964).

(7) D. S. Moss and S. P. Sinha, *Z. Phys. Chem.* (*Frankfurt am Main*), **63**, 190 (1969).