appreciate the help of Dr. Sven Westman in correcting the English of this paper. The investigation has been performed with financial support from the Tri-Centennial Fund of the Bank of Sweden and from the Swedish Natural Science Research Council. L. N. gratefully acknowledges financial aid from the Neste Oy Foundation.

Registry No. $\{(NH_4)[Sm(H_2O)_3(SO_4)_2]\cdot H_2O\}_x$, 42949-48-4; $NH_4La(SO_4)_2\cdot 4H_2O$, 42886-02-2; $NH_4Ce(SO_4)_2\cdot 4H_2O$, 10049-02-2; $NH_4Pr(SO_4)_2\cdot 4H_2O$, 13494-85-4; $NH_4Nd(SO_4)_2\cdot 4H_2O$, 42886-04-4; $NH_4Sm(SO_4)_2\cdot 4H_2O$, 34370-41-7; $NH_4Eu(SO_4)_2\cdot 4H_2O$, 14175-66-7; $NH_4Gd(SO_4)_2\cdot 4H_2O$, 25321-74-8; $NH_4Tb(SO_4)_2\cdot 4H_2O$, 15681-94-4.

Supplementary Material Available. Table III, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-290.

Contribution from Ames Laboratory—USAEC and the Department of Chemistry, Iowa State University,
Ames, Iowa 50010, and the Department of Chemistry, Youngstown State University, Youngstown, Ohio 44503

Chemistry of Polynuclear Metal Halides. XI. Crystal and Molecular Structure of Tris(tetramethylammonium) Hexachloro(dodeca-μ-chloro-hexaniobate), $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$[1]

F. W. KOKNAT[2a] and R. E. McCARLEY*[2b]

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The structure of the new compound $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$ was determined by single-crystal X-ray methods and refined to a conventional R factor $R_1 = 0.069$. The compound crystallizes in the trigonal-rhombohedral space group $R3$ with $a_{\mathrm{trig}} = 11.408 \pm 0.005$ and $c_{\mathrm{trig}} = 30.31 \pm 0.01$ Å, and three formula units in the trigonal unit cell. It contains a close-packed cubic arrangement of $[(Nb_6Cl_{12})Cl_6]^{3-}$ complex cluster anions which are based on $(Nb_6Cl_{12})^{3+}$ central cations. The tetramethylammonium cations occupy all tetrahedral and octahedral holes of this arrangement. Slight deviations of the $(Nb_6Cl_{18})^{3-}$ anion from strict octahedral symmetry are apparently caused by the packing of the $(Nb_6Cl_{18})^{3-}$ and $(CH_3)_4N^+$ units. Important average bond distances are 2.97 Å for Nb-Nb, 2.43 Å for Nb-Cl_{bridging}, and 2.52 Å for Nb-Cl_{terminal}. Comparison of these data with values reported for $K_4Nb_6Cl_{18}$ and $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$ shows that Nb-Nb distances increase gradually and that Nb-Cl_{terminal} distances decrease gradually upon stepwise removal of two electrons from an $(Nb_6Cl_{18})^{4-}$ anion. The results tend to confirm that the two electrons are taken from a bonding MO centered primarily on the metal atoms.

Introduction

Niobium and tantalum are known to form a number of lower valent halides that contain hexanuclear $(M_6X_{12})^{n+}$ cluster cations. Previous work[3] has shown that such cluster cations may occur in three different oxidation states with $n = 2$, 3, and 4. Experimental evidence for metal-metal bonding in $(M_6X_{12})^{n+}$ cations has been established by magnetic[4,5] and spectral[6-8] measurements of compounds containing M_6X_{12} units and by the short metal-metal distances found in the structures of Nb_6F_{15},[9] Nb_6Cl_{14},[10] $K_4Nb_6Cl_{18}$,[11] Ta_6Cl_{15},[12] Ta_6I_{14},[13] and $H_2[Ta_6Cl_{18}]\cdot 6H_2O$.[14]

To describe metal-metal bonding in electron-deficient $(M_6X_{12})^{n+}$ cluster cations, a molecular orbital approach is most advantageous. In a simplified MO treatment by Cotton and Haas,[15] d_{xy}, d_{xz}, d_{yz}, and d_{z^2} orbitals of all six metal atoms are combined to form 8 bonding and 16 antibonding molecular orbitals. With 16 electrons available for metal-metal bonding as in the doubly charged $(M_6X_{12})^{2+}$ cluster cation, all 8 bonding orbitals should be filled and all 16 antibonding orbitals should be vacant. Since oxidation to form clusters with $n = 3$ or 4 removes bonding electrons, an increase in the M-M bond distances under retention of the octahedral symmetry of the cluster would be anticipated.

This present work is part of a study on the influence of oxidation on the structure of the $(Nb_6Cl_{12})^{n+}$ cluster cation. The qualitative correctness of the above MO treatment may be checked by establishing if, upon oxidation of the cluster, niobium-niobium distances increase under retention of octahedral symmetry. A determination of the crystal structure of $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$,[16] which contains complex $(Nb_6Cl_{18})^{2-}$ anions based on $(Nb_6Cl_{12})^{4+}$ central cations, and a comparison of the obtained bond distances and angles with data reported for $K_4Nb_6Cl_{18}$[11] has shown that two-electron oxidation of the $(Nb_6Cl_{12})^{2+}$ unit causes a significant increase in Nb-Nb bond distances under retention of octa-

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(1) Presented at the XIIIth International Conference on Coordination Chemistry, Cracow-Zakopane, Poland, Sept 1970; see Abstract 234.

(2) (a) Youngstown State University; (b) Iowa State University.

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

(4) R. A. Mackay and R. F. Schneider, *Inorg. Chem.*, 6, 549 (1967).

(5) J. G. Converse and R. E. McCarley, *Inorg. Chem.*, 9, 1361 (1970).

(6) R. F. Schneider and R. A. Mackay, *J. Chem. Phys.*, 42, 843 (1968).

(7) B. Spreckelmeyer, *Z. Anorg. Allg. Chem.*, 365, 225 (1969).

(8) P. B. Fleming and R. E. McCarley, *Inorg. Chem.*, 9, 1347 (1970).

(9) H. Schafer, H. G. Schnering, J.-J. Niehus, and H. G. NiederVahrenholz, *J. Less-Common Metals*, 9, 95 (1965).

(10) A. Simon, H. G. Schnering, H. Wohrle, and H. Schafer, *Z. Anorg. Allg. Chem.*, 339, 155 (1965).

(11) A. Simon, H. G. Schnering, and H. Schafer, *Z. Anorg. Allg. Chem.*, 361, 235 (1968).

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

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

(14) C. B. Thaxton and R. A. Jacobson, *Inorg. Chem.*, 10, 1460 (1971).

(15) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 3, 10 (1964).

hedral symmetry. This was regarded as support for the correctness of the MO treatment.

In this paper the crystal structure of the compound $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$, which contains $(Nb_6Cl_{18})^{3-}$ complexes based on $(Nb_6Cl_{12})^{3+}$ cluster cations, is reported. The purpose of this study is to determine (1) whether or not structural changes caused by two-electron oxidation of the $(Nb_6Cl_{18})^{4-}$ anion proceed in two approximately equal steps, (2) if and to what extent the Nb_6 octahedron in the triply charged $(Nb_6Cl_{18})^{3-}$ anion is distorted, and (3) if the conclusions drawn from the MO treatment are also consistent with the experimental results obtained in this study.

Preparation of $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$

To a hot saturated solution of dry HCl gas in 150 ml of absolute ethanol was added 7.5 g (5 mmol) of $[(CH_3)_4N]_4[(Nb_6Cl_{12})Cl_6]$.[16] Addition of 635 mg (5 mequiv) of dry iodine to the mixture brought about dissolution and oxidation of the cluster material. The solution obtained was flushed with dry HCl gas, and then 10 g of dry solid tetramethylammonium chloride was added in small portions and with stirring. To complete precipitation of the product, the mixture was stirred and heated for 15 min and allowed to cool down as HCl gas was bubbled through the supernatant liquid. A 5-g amount of glittering brown plates was collected on a fritted glass filter, washed with a 3:1 mixture of absolute ethanol and chloroform, thereafter with absolute ethanol, and dried *in vacuo*. *Anal.* Calcd for $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$: Nb, 39.31; Cl, 45.00; N, 2.96; C, 10.16; H, 2.56. Found: Nb, 39.40; Cl, 44.92; N, 3.14; C, 9.35; H, 2.24; Cl:Nb, 17.93:6.00.

The compoud is completely insoluble in chloroform and carbon tetrachloride and nearly insoluble in water or ethanol. Its reflectance spectrum shows a sharp peak at 440 nm, which is characteristic of the $(Nb_6Cl_{12})^{3+}$ unit. Crystalline material obtained as described above is stable in air. Samples recrystallized from propionitrile or acetonitrile however are subject to partial decomposition in air.

Data Collection and Reduction

Weissenberg photographs revealed that the compound crystallizes in the trigonal-rhombohedral system with the plane of its plates normal to the trigonal *c* axis. No systematic extinctions except for those required for rhombohedral symmetry were observed, and the Laue symmetry was found to be 3. The lattice constants were obtained from Guinier photographs with tungsten as a standard (a = 3.15884 Å)[17] and refined by least-squares methods[18] to the final values $a_{trig} = 11.408 \pm 0.005$, $c_{trig} = 30.31 \pm 0.01$ Å, and $V_{trig} = 3416 \pm 4$ Å^3. The rhombohedral lattice constants are $a_{rhomb} = 12.06$ Å and $\alpha_{rhomb} = 56.46°$. With three formula units per trigonal unit cell and one formula unit per rhombohedral unit cell, the calculated density of 2.07 g cm^{-3} agrees with the observed density of 2.07 g cm^{-3}, measured by displacement of carbon tetrachloride.

Weissenberg photographs also revealed that the crystals were twinned, showing a superposition of two trigonal-rhombohedral lattices in such a way that for layers *hkl* with $l \neq 3n$ the reflections from one trigonal lattice coincided with half of the systematic extinctions from the other trigonal lattice, whereas layers *hkl* with $l = 3n$ did not show any obvious signs of superposition since the reflections from one lattice exactly coincided with the reflections from the other lattice. This suggests that the two lattices are rotated against each other by 60° with respect to their common *c* axis. The twin boundary in the real lattice was located normal to the trigonal *c* axis and parallel to the main plane of the platelets. It could be observed quite easily under the microscope.

In spite of considerable preparative efforts, it was not possible to obtain untwinned material. A twinned crystal had to be used for the structure determination, but this turned out to cause less difficulty than originally expected. First, two-thirds of the reflections did not coincide anyway. They could be used without any extraordinary corrections. Second, a twinned crystal was found whose major part (0.1 mm in diameter, 0.025 mm thick) was considerably larger than its unwanted counterpart. By checking corresponding reflections *hkl* with $l \neq 3n$ from both parts of the twin it was found that the reflections from the unwanted part had only 7.8% of the intensities of the equivalent reflections from the larger part of the twin. It was concluded that the same relationship would be true for reflections *hkl* with $l = 3n$, and since the contributions from the unwanted part of the twin were small, the observed intensity values for these reflections were used without any other than the usual corrections. However, in calculating standard deviations a special term was added that took care of contributions from the unwanted part of the twin. Further explanations will be given below.

Three-dimensional intensity data were taken on an automated Hilger and Watts four-circle diffractometer by a moving-crystal, moving-counter technique. Each reflection was step scanned from $\theta(\text{calcd}) - (0.25° + \theta/100)$ to $\theta(\text{calcd}) + (0.25° + \theta/100)$ at a rate of 0.4096 sec for each step of 0.01°. Stationary-background counts, each for a period equal to half of the scan time, were taken at the beginning and at the end of each scan. Zirconium-filtered Mo Kα radiation was used under a takeoff angle of *ca.* 4° to measure two complete, symmetry-related sets of data, each consisting of 1377 independent reflections within a sphere of $2\theta < 50°$. The intensities were measured with a scintillation counter equipped with a pulse height analyzer adjusted to receive 90% of the Mo Kα pulse distribution. The stability of the system, *i.e.*, crystal and electronics, was checked periodically by measuring three standard reflections after every batch of 20 data. None of the three reflections showed any systematic variation of intensity.

The observed intensities were corrected for Lorentz and polarization effects in the usual way and for absorption using a local version of the Busing and Levy absorption correction program.[18] Calculated transmission factors *A* varied from 0.82 to 0.91. The linear absorption correction coefficient for Mo Kα radiation is 24.72 cm^{-1}.

The obtained intensities were averaged over the two symmetry-related sets of data. Standard deviations for the averaged intensities of 914 "untwinned" reflections (*hkl* with $l \neq 3n$) were estimated by

$$\sigma(I_{av}) = [(TC_{max} - TC_{min})^2/N + (BG_{max} - BG_{min})^2/N + (P(BG))^2 + (P(TC))^2]^{1/2}$$

where N is the number of times a reflection or its equivalent was measured, TC is the total count, BG is the background count, and I is TC − BG; P was set to 0.05. In the above equation, $(TC_{max} - TC_{min})^2$ was replaced by TC_{av} if TC_{av} was larger, and $(BG_{max} - BG_{min})^2$ was replaced by BC_{av} if BG_{av} was larger. To obtain $\sigma(F_o)$, the equation $\sigma(F_o) = [(I + \sigma(I))/A(Lp)]^{1/2}$ was used.[19] "Twinned" reflections were divided into two groups which were treated in two different ways. A set of 27 reflections *hk*0 and their own equivalents from the smaller part of the twin coincided with each other. These were treated in the same way as untwinned reflections except that they were refined on with their own, independent scale factor. The remaining 436 reflections *hkl* with $l = 3n$ coincided with reflections $\overline{hk}l$ from the smaller, unwanted part of the twin in such a way that interference could occur. Since reflections from the smaller, unwanted part of the twin had only 7.8% of the intensities of their equivalents from the larger part of the twin, intensity values without any extraordinary corrections were used. However, for the calculation of $\sigma(I_{av})$ a fourth term $(0.078I_{av}(\overline{hk}l))^2$ was added within the bracket to take into account the contribution from the unwanted part of the twin. A total of 969 averaged F_o values with $F_o > 2\sigma(F_o)$ were considered observed and used for the solution and refinement of the structure.

Solution and Refinement of the Structure

A Harker synthesis parallel to 001 revealed the orientation of the $(Nb_6Cl_{18})^{3-}$ cluster anion in the trigonal lattice. The rest of the structure was solved by full-matrix least-squares procedures and by Fourier calculations.[18] Scattering factors for $Nb^{2.50+}$ were interpolated from tables given by Thomas and Umeda.[20] Values used for N and C were those given by Hanson, Herman, Lea, and Skilman,[21] while the scattering factor for Cl^- and anomalous dispersion corrections for Nb and

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(16) F. W. Koknat and R. E. McCarley, *Inorg. Chem.*, 11, 812 (1972).

(17) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(18) All computations were performed on an IBM 360/50 or 360/65 computer using the following programs: lattice constant refinement program, local program written by the authors; the absorption correction program for polyhedral crystals by Busing and Levy, ABCO; intensity data reduction program, local program by authors; two- and three-dimensional Patterson, Fourier, and difference Fourier programs by the authors; the Busing, Martin, and Levy programs for least-squares refinement (ORFLS) and crystallographic function and error program (ORFFE); and the Johnson thermal ellipsoid plotting program, ORTEP.

(19) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 7, 2124 (1968).

(20) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, 26, 293 (1957).

(21) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

Table I. Final Positional and Thermal Parameters[a] for $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$

Atom	10^4x	10^4y	10^4z	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Cl(1)	1871 (12)	3522 (8)	−0011 (3)	0124 (13)	0045 (8)	0009 (1)	0039 (8)	−0006 (3)	−0010 (2)
Cl(2)	−1816 (12)	−3352 (10)	−0016 (5)	0077 (11)	0057 (9)	0028 (2)	0020 (9)	0009 (4)	0013 (3)
Cl(3)	−1668 (16)	0118 (13)	0909 (6)	0152 (18)	0127 (18)	0026 (2)	0065 (16)	0007 (5)	−0003 (5)
Cl(4)	1714 (9)	−0050 (9)	−0920 (3)	0066 (9)	0066 (9)	0006 (1)	0035 (8)	0004 (2)	0000 (2)
Cl(5)	3205 (15)	−0193 (13)	0857 (5)	0143 (15)	0088 (11)	0018 (2)	0043 (11)	−0013 (4)	−0006 (4)
Cl(6)	−3234 (11)	0088 (14)	−0910 (4)	0066 (11)	0145 (14)	0021 (2)	0067 (11)	−0013 (3)	0007 (4)
Nb(1)	1453 (4)	−0069 (4)	0400[b]	0075 (4)	0073 (4)	0011 (1)	0040 (3)	−0004 (1)	−0009 (1)
Nb(2)	−1479 (4)	0065 (4)	−0401 (1)	0071 (4)	0079 (4)	0016 (1)	0040 (4)	−0002 (1)	0010 (1)

Group[e]	Atom	x	y	z	ϕ^c	θ^c	ρ^c	B, Å^2
1		0	0	0.2146 (10)	0.3 (17)	0	0	5.2 (7)
	C(1)	1.394	0	−0.493				
	C(4)	0	0	1.479				
	N(1)[d]	0	0	0				
2		0	0	−0.2249 (10)	−0.1 (18)	0	0	5.5 (8)
	C(2)	−1.394	0	0.493				
	C(5)	0	0	−1.479				
	N(2)[d]	0	0	0				
3		0	0	−0.4714 (12)	3.2 (25)	0	0	10.2 (10)
	C(3)	1.394	0	−0.493				
	C(6)	0	0	1.479				
	N(3)[d]	0	0	0				

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. [b] The z parameter of Nb(1) was held constant. [c] For a definition of angles see C. Scheringer, *Acta Crystallogr.*, 16, 546 (1963). [d] Nitrogen atoms were taken as the origins of the rigid groups. [e] x, y, and z in Å; ϕ, θ, and ρ in radians.

Cl were taken from ref 17. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with $w = [\sigma(F_o)]^{-2}$. Tetramethylammonium cations were refined as rigid, strictly tetrahedral groups with d_{C-N} equal to 1.479 Å.

With the absence of systematic extinctions except for those required for rhombohedral symmetry and the diffraction symmetry $\bar{3}$, the possible space groups were R3 and $R\bar{3}$. Approximate Nb and Cl positions obtained from the Harker map and isotropic temperature factors arbitrarily set equal to 3 were used to start the least-squares refinement in the centrosymmetric space group $R\bar{3}$. Two cycles of refinement of these parameters led to an unweighted R factor, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.158 and to a weighted R factor, $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.176. A difference Fourier synthesis of the plane 100 revealed the positions of two of the three tetramethylammonium cations, and four subsequent cycles of refinement, two of them with fixed tetramethylammonium parameters, lowered R_1 to 0.139 and R_2 to 0.144. At this stage a difference Fourier synthesis revealed the location of the third $(CH_3)_4N^+$ group, either in an unambiguous position of the noncentrosymmetric space group $R3$, or in a statistically disordered state with an occupancy factor of 0.5 in a position of space group $R\bar{3}$. It seemed that the unambiguous position was more likely, and the refinement was therefore completed in the noncentrosymmetric space group $R3$. The choice of $R3$ over $R\bar{3}$ was confirmed by an application of Hamilton's R factor ratio test[22] which showed that restriction to the centrosymmetric space group $R\bar{3}$ was not significant at the 99.5% confidence level. Inclusion of the third $(CH_3)_4N^+$ group improved R_1 to 0.131 and R_2 to 0.134, and four cycles of refinement with fixed parameters for the tetramethylammonium cations brought a reduction to $R_1 = 0.121$ and $R_2 = 0.125$. Four additional cycles of refinement on all parameters brought an improvement to $R_1 = 0.119$ and $R_2 = 0.123$. A change to anisotropic temperature factors for Nb and Cl in the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and eight additional cycles of refinement, five of them with fixed tetramethylammonium groups, reduced R_1 to 0.069 and R_2 to 0.073. At this point it was discovered that some C–Cl distances involving carbon atoms from two of the three tetramethylammonium groups were unreasonably small. The coordinates of all three tetramethylammonium groups were rechosen by inverting them through the pseudoinversion center[23] located in the center of the $(Nb_6Cl_{18})^{3-}$ group. This brought about a considerable improvement in the C–Cl distances. Three additional cycles of refinement gave the final R factor values $R_1 = 0.069$ and $R_2 = 0.072$. The largest shift in the last cycle of refinement was 0.24 esd; the final standard error for an observation of unit weight was 0.87. A final difference Fourier map showed no peaks larger than 0.80 e Å^{-3}.

An R factor ratio test[22] to determine the absolute configuration was not conclusive. The reason for this is apparently the pseudocentrosymmetric arrangement of the cluster anion and of two of the three tetramethylammonium cations. The configuration originally used in the refinement gave the more reasonable interatomic distances and was therefore kept. Final positional and thermal parameters are given in Table I. For reasons of clarity, the $(Nb_6Cl_{18})^{3-}$ cluster anion has been centered in the origin of the trigonal lattice.

Description and Discussion of the Structure

In this structure both $(Nb_6Cl_{18})^{3-}$ cluster anions and tetramethylammonium cations are centered on the threefold axes. The large $(Nb_6Cl_{18})^{3-}$ anions form an approximately close-packed cubic arrangement and the tetramethylammonium cations occupy all tetrahedral and all octahedral holes. The arrangement of anions and cations parallel to (001) of the trigonal lattice is partially shown in Figure 1. Niobium atoms Nb(1) and Nb(2), terminal chlorine atoms Cl(5) and Cl(6), axial bridging chlorine atoms Cl(3) and Cl(4), and the carbon atoms C(1), C(2), and C(3) are located in positions very close to the faces 100 of the trigonal unit cell. Equatorial bridging chlorine atoms Cl(1) and Cl(2) occupy positions that are almost on the planes 110. Since octahedral holes in a close-packed arrangement are roughly 4 times as large as tetrahedral holes, the tetramethylammonium ions fill only a small part of the octahedral holes. The empty space left in the octahedral holes is an interesting feature of this structure, which is consistent with the relatively low density of the compound and the high-temperature factor found for the third tetramethylammonium group.

A single $(Nb_6Cl_{18})^{3-}$ anion is shown in Figure 2, and important interatomic distances and angles are given in Table II. The cluster unit deviates slightly from ideal octahedral symmetry, apparently due to the stacking of cluster anions and tetramethylammonium cations. From their "ideal" orientations with Nb(1), Nb(2), Cl(3), Cl(4), Cl(5), and Cl(6) on the faces 100 of the trigonal unit cell the clusters are rotated slightly clockwise. This causes an increase in volume of the tetrahedral holes and a decrease in volume of the octahedral holes. The clockwise rotation is larger for atoms of the upper halves of the cluster units, *i.e.*, Nb(1), Cl(3), and Cl(5), and this decreases the volume of the empty lower halves of the octahedral holes. The twisting of the cluster units leads

(22) W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

(23) Compare G. D. Sproul and G. D. Stucky, *Inorg. Chem.*, 11, 1647 (1972).

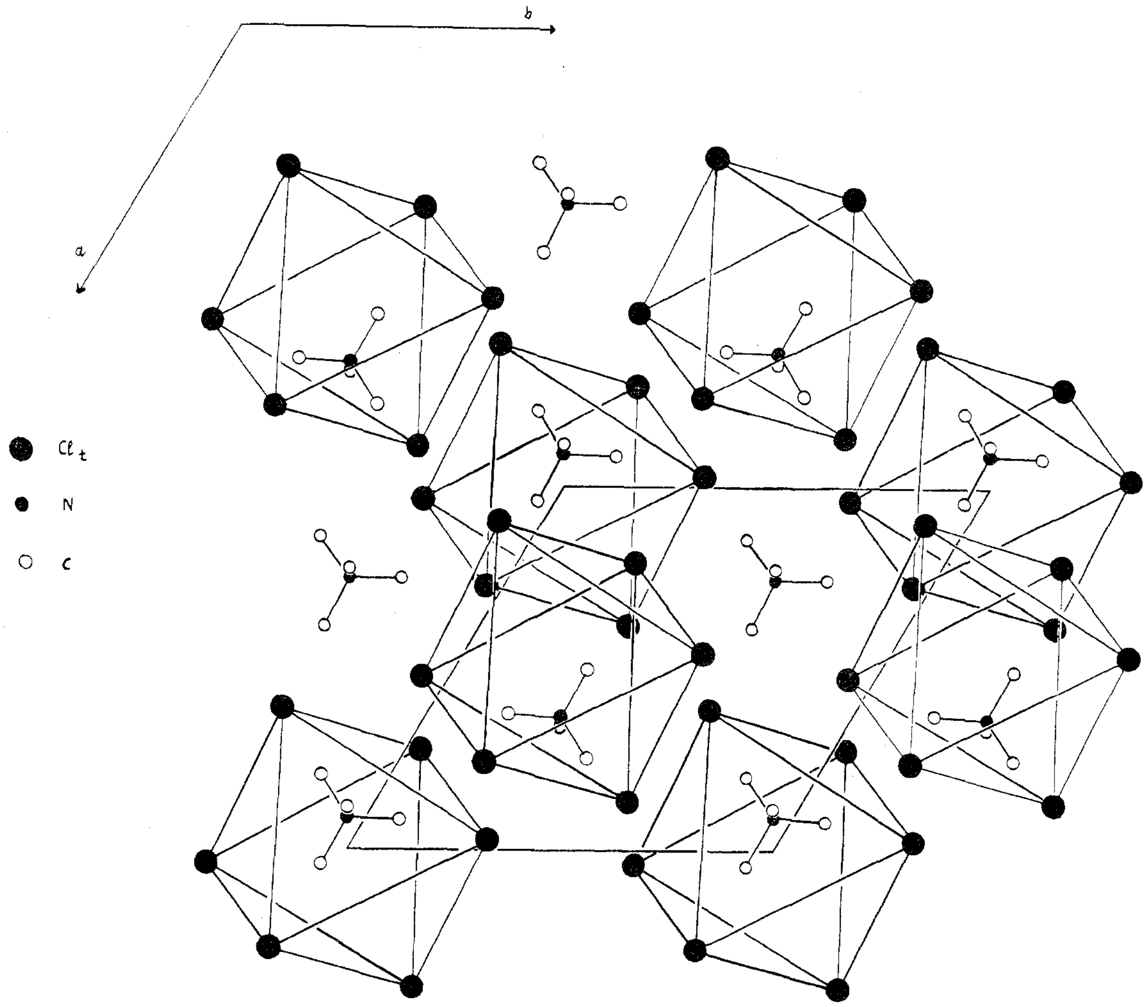

Figure 1. The arrangement of tetramethylammonium ions between two close-packed layers of $[(Nb_6Cl_{12})Cl_6]^{3-}$ cluster anions as seen in the [001] projection. In this view the trigonal *c* axis is tilted a few degrees from the direction perpendicular to the plane of the figure. Only terminal chlorine atoms of the cluster anion are shown.

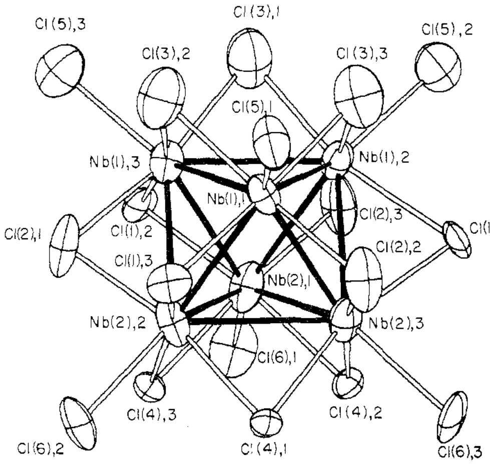

Figure 2. The structure of the $[(Nb_6Cl_{12})Cl_6]^{3-}$ cluster anion.

to two different Nb(1)-Nb(2) bond distances, 2.967 and 2.972 Å. The most striking deviation from strict octahedral symmetry however is a downward shift of the terminal chlorine atoms Cl(5) and Cl(6). Apparently the tetrahedral holes in this structure are somewhat small for the tetramethylammonium groups, and lateral pressure from carbon atoms C(1) forces terminal chlorine atoms Cl(6) to leave their "ideal" positions and move downward parallel to the trigonal *c* axis into the octahedral holes. Terminal chlorine atoms Cl(5), in a likewise crowded situation with carbon atoms C(2), cannot move upward into the octahedral holes since they are in an eclipsed configuration with carbon atoms C(3) from the tetramethylammonium groups that occupy the octahedral holes. Instead, they move downward toward the "equator" of the cluster, thereby pressing together niobium atoms Nb(1). As a result, niobium-terminal chlorine and niobium-niobium distances differ noticeably. They are 2.494 Å for Nb(1)-Cl(5), 2.540 Å for Nb(2)-Cl(6), 2.942 Å for Nb(1)-Nb(1), and 2.989 Å for Nb(2)-Nb(2).

Of particular interest in this study is the effect of oxidation on the structure of the $(Nb_6Cl_{18})^{n-}$ anion, which can be evaluated by a comparison of bond distances and angles in the threefold negative anion of $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$ with corresponding data for the fourfold and twofold negative anions of $K_4Nb_6Cl_{18}$[11] and $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$[16] as given in Table III. Also contained in Table III are bond distances and angles for Nb_6Cl_{14}[10] and for $(pyH)_2Nb_6Cl_{18}$.[24] A comparison of the data for $[(CH_3)_4N]_2Nb_6Cl_{18}$ and $(pyH)_2$-Nb_6Cl_{18} which contain the same $(Nb_6Cl_{18})^{2-}$ anion shows that the cations in these compounds apparently have some influence on bond distances and angles in the Nb_6Cl_{18} complex anion. The following discussion will therefore be based on data for $[(CH_3)_4N]_2Nb_6Cl_{18}$ and $[(CH_3)_4N]_3Nb_6Cl_{18}$,

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(24) B. Spreckelmeyer and H. G. Schnering, *Z. Anorg. Allg. Chem.*, 386, 27 (1971).

Table II. Interatomic Distances (Å) and Angles (deg) in $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$[a,b]

Intramolecular Interatomic Distances	
Nb(1),1–Nb(1),2	2.942 (7)
Nb(1),1–Nb(2),2	2.967 (4)
Nb(1),1–Nb(2),3	2.972 (5)
Nb(2),1–Nb(2),2	2.989 (7)
Nb(1),1–Nb(2),1	4.197 (3)
Nb(1),1–Cl(1),3	2.51 (1)
Nb(1),1–Cl(2),2	2.38 (1)
Nb(1),1–Cl(3),2	2.43 (2)
Nb(1),1–Cl(3),3	2.39 (2)
Nb(2),1–Cl(1),2	2.47 (1)
Nb(2),1–Cl(2),3	2.34 (1)
Nb(2),1–Cl(4),2	2.43 (1)
Nb(2),1–Cl(4),3	2.46 (1)
Nb(1),1–Cl(5),1	2.49 (1)
Nb(2),1–Cl(6),1	2.54 (1)
Cl(1),1–Cl(2),2	3.44 (2)
Cl(1),1–Cl(2),3	3.37 (2)
Cl(1),1–Cl(3),3	3.47 (2)
Cl(1),1–Cl(4),2	3.43 (1)
Cl(2),1–Cl(3),2	3.37 (2)
Cl(2),1–Cl(4),3	3.30 (2)
Cl(3),1–Cl(3),2	3.42 (3)
Cl(4),1–Cl(4),2	3.44 (2)
Cl(5),1–Cl(1),3	3.22 (2)
Cl(5),1–Cl(2),2	3.25 (2)
Cl(5),1–Cl(3),2	3.29 (2)
Cl(5),1–Cl(3),3	3.26 (2)
Cl(6),1–Cl(1),2	3.29 (2)
Cl(6),1–Cl(2),3	3.34 (2)
Cl(6),1–Cl(4),2	3.25 (1)
Cl(6),1–Cl(4),3	3.24 (2)
Cl(5),1–Cl(5),2	6.53 (3)
Cl(5),1–Cl(6),2	6.49 (2)
Cl(5),1–Cl(6),3	6.59 (2)
Cl(6),1–Cl(6),2	6.48 (2)
Cl(5),1–Cl(6),1	9.23 (1)
Closest Anion–Anion Contacts	
Cl(3)–Cl(6)	4.98 (2)
Cl(5)–Cl(4)	5.13 (2)
Cl(1)–Cl(1)	5.39 (2)
Cl(2)–Cl(2)	5.68 (2)
Cl(5)–Cl(6)	6.04 (2)
Cl(5)–Cl(6)	6.21 (1)
Closest Anion–Cation Contacts	
Cl(5)–C(3)	3.62
Cl(3)–C(1)	3.66
Cl(6)–C(1)	3.67
Cl(5)–C(2)	3.68
Cl(6)–C(1)	3.69

Intramolecular Angles	
Nb(1),2–Nb(1),1–Nb(2),3	60.2 (1)
Nb(1),3–Nb(1),1–Nb(2),2	60.4 (1)
Nb(2),2–Nb(1),1–Nb(2),3	60.4 (2)
Nb(2),2–Nb(2),1–Nb(1),3	59.9 (1)
Nb(2),3–Nb(2),1–Nb(1),2	59.7 (1)
Nb(1),2–Nb(2),1–Nb(1),3	59.4 (2)
Nb(1),2–Nb(1),1–Nb(2),2	90.5 (2)
Nb(1),3–Nb(1),1–Nb(2),3	90.4 (1)
Nb(2),2–Nb(2),1–Nb(1),2	89.5 (1)
Nb(2),3–Nb(2),1–Nb(1),3	89.6 (1)
Cl(5),2–Cl(5),1–Cl(6),3	59.3 (2)
Cl(5),3–Cl(5),1–Cl(6),2	60.8 (3)
Cl(6),2–Cl(5),1–Cl(6),3	59.4 (2)
Cl(6),2–Cl(6),1–Cl(5),3	61.1 (2)
Cl(6),3–Cl(6),1–Cl(5),2	59.5 (2)
Cl(5),2–Cl(6),1–Cl(5),3	59.9 (3)
Cl(5),2–Cl(5),1–Cl(6),2	90.2 (2)
Cl(5),3–Cl(5),1–Cl(6),3	89.3 (2)
Cl(6),2–Cl(6),1–Cl(5),2	89.8 (2)
Cl(6),3–Cl(6),1–Cl(5),3	90.7 (2)
Cl(5),1–Nb(1),1–Nb(2),1	178.1 (4)
Cl(6),1–Nb(2),1–Nb(1),1	177.5 (3)
Cl(1),3–Nb(1),1–Cl(3),3	163.5 (4)
Cl(2),2–Nb(1),1–Cl(3),2	167.3 (5)
Cl(1),2–Nb(2),1–Cl(4),2	163.6 (4)
Cl(2),3–Nb(2),1–Cl(4),3	167.0 (4)
Cl(1),3–Nb(1),1–Cl(2),2	87.0 (6)
Cl(1),3–Nb(1),1–Cl(3),2	89.3 (5)
Cl(2),2–Nb(1),1–Cl(3),3	89.9 (5)
Cl(3),2–Nb(1),1–Cl(3),3	90.3 (8)
Cl(1),2–Nb(2),1–Cl(2),3	91.2 (6)
Cl(1),2–Nb(2),1–Cl(4),3	88.2 (4)
Cl(2),3–Nb(2),1–Cl(4),2	87.6 (4)
Cl(4),2–Nb(2),1–Cl(4),3	89.4 (4)
Cl(1),3–Nb(1),1–Cl(5),1	79.9 (4)
Cl(2),2–Nb(1),1–Cl(5),1	83.7 (5)
Cl(3),2–Nb(1),1–Cl(5),1	83.7 (5)
Cl(3),3–Nb(1),1–Cl(5),1	83.6 (5)
Cl(1),2–Nb(2),1–Cl(6),1	82.1 (4)
Cl(2),3–Nb(2),1–Cl(6),1	86.3 (5)
Cl(4),2–Nb(2),1–Cl(6),1	81.5 (4)
Cl(4),3–Nb(2),1–Cl(6),1	80.8 (4)
Nb(1),1–Cl(3),3–Nb(1),2	75.2 (5)
Nb(2),1–Cl(4),3–Nb(2),2	75.4 (3)
Nb(1),1–Cl(1),3–Nb(2),2	73.2 (2)
Nb(1),1–Cl(2),2–Nb(2),3	78.0 (3)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled as in Figure 2.

which contain the same cation, and on data for $K_4Nb_6Cl_{18}$, which is so far the only compound with an $(Nb_6Cl_{18})^{4-}$ anion whose structure has been determined.

In an Nb_6Cl_{18} unit, each niobium atom is surrounded by an approximately square-planar group of four bridging chlorine atoms, Cl_b. The metal atom is not situated exactly in the center of this group, but slightly below the plane of the four chlorine atoms. Therefore it is difficult for the fifth chlorine, Cl_t, to approach the niobium atom. Instead of having a sixth chlorine nearest neighbor like a metal ion in a regular ionic compound, each niobium atom is bonded by the other niobium atoms of the cluster. The metal-metal bonding in these electron-deficient metal cluster units is best described by a molecular orbital treatment.

In an $(Nb_6Cl_{18})^{4-}$ unit as in $K_4Nb_6Cl_{18}$, 16 electrons are available for metal-metal bonding. They can be accommodated by the 8 bonding molecular orbitals proposed in a simplified MO treatment by Cotton and Haas.[15] With a threefold negative charge on the Nb_6Cl_{18} cluster anion as in $[(CH_3)_4N]_3Nb_6Cl_{18}$, 15 electrons are available for metal-metal bonding, and only 14 electrons in the $(Nb_6Cl_{18})^{2-}$ anion of $[(CH_3)_4N]_2Nb_6Cl_{18}$.

One- and two-electron oxidation of the $(Nb_6Cl_{18})^{4-}$ cluster anion results in an increase of the Nb–Nb bond distances in two equal steps from 2.92 to 2.97 to 3.02 Å under retention of octahedral symmetry. This indicates that the ionized electrons are removed from bonding orbitals centered mainly on the M_6 cluster. Since $(Nb_6Cl_{12})^{2+}$ and $(Nb_6Cl_{12})^{4+}$ cations are diamagnetic and since $(Nb_6Cl_{12})^{3+}$ cations show a paramagnetism corresponding to one unpaired electron,[5] these electrons are removed from the same orbital.

Because oxidation of the cluster raises the formal oxidation number of each niobium atom from 2.33+ in $(Nb_6Cl_{18})^{4-}$ to 2.50+ in $(Nb_6Cl_{18})^{3-}$ to 2.67+ in $(Nb_6Cl_{18})^{2-}$, a significant shortening of the Nb–Cl bond distances would be anticipated in this series. This has been found to be the case for the terminal chlorine atoms; Nb–Cl_t bond distances decrease from 2.61 to 2.52 to 2.46 Å as the oxidation number increases. Since shorter interatomic distances are generally associated with stronger bonds, it would appear that upon oxidation of the cluster the Nb–Cl_t bond is considerably strengthened. However, the Nb–Cl_t distances in all of these clusters are longer than the respective Nb–Cl_b distances and also longer than the estimated normal covalent bond distance of 2.35–2.40 Å. Therefore, even the strongest Nb–Cl_t bonds in the clusters appear to be relatively weak.

The relative weakness of the Nb–Cl_t bonds may be attributed to the geometry of the Nb_6Cl_{18} cluster unit. Since the niobium atom is located below the plane of its four Cl_b neighbors, it is sterically difficult for the terminal chlorine to get sufficiently close to the niobium atom. Changes in Nb–Nb bond distances caused by oxidation of the cluster have quite an impact on the position of each niobium atom with respect to its set of four bridging chlorine atoms. Upon oxidation of the cluster unit, the Cl_b–Nb–Cl_b bond angle across the plane increases from 161.9 to 165.6 to 167.2°, and the niobium atom moves up from 0.39 to 0.31 to 0.27 Å below the plane of its four bridging chlorine atoms. Hence, the niobium atom becomes more accessible to the terminal chlorine atom, and the Nb–Cl_t bond is considerably strengthened upon oxidation of the cluster unit.

The weakness of the Nb–Cl_t bond in the $(Nb_6Cl_{18})^{3-}$ and $(Nb_6Cl_{18})^{4-}$ anions is also suggested by the fact that there are two significantly different Nb–Cl_t bond distances in both $[(CH_3)_4N]_3Nb_6Cl_{18}$ (2.49 and 2.54 Å) and $K_4Nb_6Cl_{18}$ (2.54 and 2.65 Å). Slight differences in the distribution of positive ions in the vicinity of terminal chlorine atoms apparently are able to cause significant differences in Nb–Cl_t bond distances.

Since the environment of the terminal chlorine atom seems to exert such a great influence on the Nb–Cl_t bond distance and since the terminal chlorine atom is more attracted by the small potassium ion than by the large tetramethylammonium cation, it does not appear quite appropriate to compare the Nb–Cl_t bond distances in the two tetramethylammonium compounds with the corresponding bond length in $K_4Nb_6Cl_{18}$. If however the Nb–Cl_t bond length of 2.58 Å from Nb_6Cl_{14},[10] which contains the same $(Nb_6Cl_{12})^{2+}$ cation as $K_4Nb_6Cl_{18}$, is used for a comparison, it can be seen that

Table III. Average Interatomic Distances (Å) and Angles (deg) in Compounds Containing $(Nb_6Cl_{12})^{n+}$ Cations

	Nb_6Cl_{14}[a]	$K_4Nb_6Cl_{18}$[b]	$[(CH_3)_4N]_3Nb_6Cl_{18}$	$[(CH_3)_4N]_2Nb_6Cl_{18}$[c]	$(pyH)_2Nb_6Cl_{18}$[d]
Cluster cation	$(Nb_6Cl_{12})^{2+}$	$(Nb_6Cl_{12})^{2+}$	$(Nb_6Cl_{12})^{3+}$	$(Nb_6Cl_{12})^{4+}$	$(Nb_6Cl_{12})^{4+}$
d(Nb-Nb), Å	2.92	2.92	2.97	3.02	3.05
d($Nb-Cl_b$),[e] Å	2.42	2.48	2.43	2.42	2.43
d($Nb-Cl_t$),[f] Å	2.58[g]	2.61	2.52	2.46	2.48
d(Cl_b-Cl_b), Å		3.46	3.40	3.40	3.42
d(Cl_b-Cl_t), Å		3.31	3.27	3.25	3.28
d(center-Nb),[h] Å	2.06	2.06	2.10	2.13	2.15
d(center-Cl_b),[h] Å	3.40	3.46	3.40	3.40	
d(center-Cl_t),[h] Å	4.67[g]	4.67	4.61	4.59	
d(Cl_b plane-Nb),[i] Å	0.35	0.39	0.31	0.27	
$Cl_b-Nb-Cl_b$, deg		161.9	165.4	167.2	
$Cl_b-Nb-Cl_b$, deg		88.6	89.1	89.3	
$Cl_b-Nb-Cl_t$, deg		81.0	82.7	83.6	
$Nb-Cl_b-Nb$, deg		71.9	75.4	77.2	

[a] Values computed from data given in ref 10. [b] Values computed from data given in ref 11. [c] Values from ref 16. [d] Values from ref 24. [e] Cl_b indicates bridging chlorine. [f] Cl_t indicates terminal chlorine. [g] Only chlorine atoms without a double function as bridging and terminal halogens have been used to calculate these values. [h] Distance from center of cluster to indicated atom. [i] Distance from metal atom to plane formed by four nearest bridging Cl atoms.

upon oxidation of the cluster the $Nb-Cl_t$ bond distance shrinks in two equal steps from 2.58 to 2.52 to 2.46 Å. This is a considerable shortening which would correspond to a decrease of about 0.36 Å in the $Nb-Cl_t$ bond length for a full one-electron oxidation of an individual niobium atom. Since ionic radii of divalent metal cations generally decrease by only 0.10-0.20 Å upon one-electron oxidation, it is obvious that the increase in the formal oxidation number of the niobium atoms is not the only reason for the observed shortening of the $Nb-Cl_t$ bonds. Certainly the above-mentioned changes in the geometry of the cluster that are caused by oxidation have a great influence on the $Nb-Cl_t$ bond length. However, it is quite possible that additional factors like slight changes in the hybridization of the niobium atoms are also involved.

$Nb-Cl_b$ bond distances seem to exhibit a somewhat unusual behavior. The average $Nb-Cl_b$ bond length for $K_4Nb_6Cl_{18}$ (2.48 Å) is considerably larger than the corresponding values of 2.43 (actually 2.42_6) and 2.42 Å found for $[(CH_3)_4N]_3Nb_6Cl_{18}$ and for $[(CH_3)_4N]_2Nb_6Cl_{18}$, respectively. Since the average $Nb-Cl_b$ bond length in Nb_6Cl_{14} is only 2.42 Å, it appears that the large $Nb-Cl_b$ bond distance in $K_4Nb_6Cl_{18}$ is due to the presence of the relatively small potassium ions. This is supported by the fact that the average distance from the center of the cluster to the bridging chlorine atoms is 3.46 Å for $K_4Nb_6Cl_{18}$ and 3.40 Å for the other three compounds. If the $Nb-Cl_b$ bond distance of 2.42 Å from Nb_6Cl_{14} rather than the value of 2.48 Å from $K_4Nb_6Cl_{18}$ is used for a comparison, it appears that oxidation of the cluster unexpectedly has practically no influence on the $Nb-Cl_b$ bond length. Apparently only the $Nb-Cl_t$ bonds, not the $Nb-Cl_b$ bonds, benefit from the loss in Nb-Nb bonding strength caused by oxidation of the cluster unit.

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Registry No. $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$, 39449-25-7; $[(CH_3)_4N]_4[(Nb_6Cl_{12})Cl_6]$, 39449-26-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-295.