

CONTRIBUTION NO. 2940 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA 50010

## Chemistry of Polynuclear Metal Halides. IX. The Crystal and Molecular Structure of Bis(tetramethylammonium)

### Hexachloro(dodeca- $\mu$ -chloro-hexaniobate), $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{1-}$

BY F. W. KOKNAT AND R. E. MCCARLEY\*

Received January 27, 1971

The structure of  $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$  has been determined by three-dimensional single-crystal X-ray analysis. The compound crystallizes in the trigonal space group  $P\bar{3}m1$  ( $D_{3d}^3$ ) with unit cell dimensions  $a = 10.850 \pm 0.005$  and  $c = 8.615 \pm 0.005$  Å. With one formula unit per unit cell the calculated density of 2.54 g/cm<sup>3</sup> is in good agreement with the measured density of 2.52 g/cm<sup>3</sup>. The derived structure was refined by least-squares methods to a conventional  $R$  index of 0.043. The  $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$  anions are located at the corners of the unit cell with the threefold axis of the octahedral cluster directed along the  $c$  axis. Though only  $D_{3d}$  symmetry is required, the metal-metal bonded octahedron of niobium atoms within the anion is not detectably distorted from  $O_h$  symmetry. Departure of the chlorine atoms from cubic symmetry is slight and probably results from packing forces within the crystals. Important intramolecular bond distances found for the anion are Nb-Nb, 3.018 (2) Å, Nb-Cl (bridging), 2.425 (2) and 2.412 (2) Å, Nb-Cl (terminal), 2.457 (3) Å. Comparison of these data with bond distances reported for  $\text{K}_4\text{Nb}_6\text{Cl}_{18}$  (A. Simon, H. G. Schnering, and H. Schäfer, *Z. Anorg. Allg. Chem.*, **361**, 235 (1968)) show that the Nb-Nb distance becomes longer, and the Nb-Cl (terminal) distance much shorter, upon removing two electrons from  $\text{Nb}_6\text{Cl}_{18}^{4-}$  to form  $\text{Nb}_6\text{Cl}_{18}^{2-}$ . These results are taken as confirmation that the two electrons are removed from a bonding MO centered primarily on the metal atoms.

#### Introduction

Previous studies<sup>2</sup> have established that the metal halide cluster species  $(\text{M}_6\text{X}_{12})^{n+}$ , where  $\text{M} = \text{Nb}$  or  $\text{Ta}$  and  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ , can be obtained in three different oxidation states with  $n = 2, 3$ , or  $4$ . Adequate experimental evidence also has been obtained to confirm the expected metal-metal bonding in these clusters. In this regard the short metal-metal internuclear distances found in the structures of  $(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2$ ,<sup>3</sup>  $\text{K}_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ ,<sup>4</sup>  $(\text{Ta}_6\text{I}_{12})\text{I}_2$ ,<sup>5</sup> or  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_3$ <sup>6</sup> and the effects of valence electron delocalization observed in the magnetic properties<sup>7,8</sup> and electronic spectra<sup>9-11</sup> of various derivatives constitute the most convincing evidence.

A crude MO treatment of the  $\text{M}_6\text{X}_{12}$  clusters has shown that of the 24 d orbitals available for metal-metal bonding within the octahedral cluster 8 should be bonding and 16 should be antibonding.<sup>12</sup> Thus, if this result is correct, the clusters with  $n = 2$  should have the 8 bonding MO's filled (16 electrons) and all antibonding orbitals vacant. Oxidation to form the clusters with  $n = 3$  or  $4$  should result in removal of one or two electrons from the bonding MO of highest energy. Because a change in the number of bonding electrons should result in an inverse change in the metal-metal bond distance, verification of the crude MO picture was sought in a comparison of structural data from similar compounds which differ principally in the oxidation state of the cluster species. In this

work the structure of  $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ , which contains the  $(\text{Nb}_6\text{Cl}_{12})^{4+}$  species, was determined for comparison with the previously published structure of  $\text{K}_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ ,<sup>4</sup> which contains the  $(\text{Nb}_6\text{Cl}_{12})^{2+}$  species.

#### Experimental Section

**Preparation of  $[(\text{CH}_3)_4\text{N}]_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ .**—To a filtered solution containing 6 g of  $(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 8\text{H}_2\text{O}$  in absolute ethanol was added 5 g of  $(\text{CH}_3)_4\text{NCl}$ , and the mixture was refluxed for 24 hr. After decanting the supernatant liquid 200 ml of absolute ethanol and 5 g of  $(\text{CH}_3)_4\text{NCl}$  were added to the dark precipitate, and the refluxing was resumed for 24 hr. The latter procedure was repeated once more, and after the final 24 hr of refluxing the dark solid was filtered, washed with absolute ethanol and chloroform, and dried *in vacuo*. The infrared spectrum of this compound was reported previously.<sup>13</sup> *Anal.* Calcd for  $[(\text{CH}_3)_4\text{N}]_4\text{Nb}_6\text{Cl}_{18}$ : Nb, 37.36; Cl, 42.77; N, 3.75; C, 12.88; H, 3.24. Found: Nb, 37.28; Cl, 42.54; N, 3.82; C, 12.78; H, 3.27; Nb:Cl = 6:17.94.

**Preparation of  $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ .**—To a saturated solution of dry HCl gas in 150 ml of absolute ethanol was added 6.5 g of  $[(\text{CH}_3)_4\text{N}]_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$  (see above). Upon bubbling dry chlorine gas through the mixture for about 1 min the starting material was completely dissolved and oxidized. The resulting solution was flushed with dry HCl gas, and 2.5 g of  $(\text{CH}_3)_4\text{NCl}$  was added in small portions. To complete precipitation of the product the mixture was heated for 10 min and allowed to cool while bubbling HCl gas through the supernatant solution. The glittering black air-stable needles (5 g) were collected on a fritted-glass filter, washed twice with a 3:1 mixture of absolute ethanol and chloroform, washed further with absolute ethanol, and dried *in vacuo*. Crystals up to 0.4 mm long and 0.1 mm in diameter could be obtained by the above procedure, if the initial solution (containing less  $(\text{CH}_3)_4\text{NCl}$ ) was seeded with a few crystals of the product. *Anal.* Calcd for  $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ : Nb, 41.48; Cl, 47.49; N, 2.08; C, 7.15; H, 1.80. Found: Nb, 41.52; Cl, 47.57; N, 2.18; C, 6.72; H, 1.48.

The success of the above preparation depends upon using  $[(\text{CH}_3)_4\text{N}]_4[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$  as the starting material. In several attempts to use  $(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 8\text{H}_2\text{O}$  as starting material the products approached the composition of  $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ , but Cl:Nb ratios of ca. 2.8-2.9 always were obtained. Guinier patterns showed that these products definitely were not identical with pure  $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ .

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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

(3) A. Simon, H. G. Schnering, H. Wöhrle, and H. Schäfer, *Z. Anorg. Allg. Chem.*, **339**, 155 (1965).

(4) A. Simon, H. G. Schnering, and H. Schäfer, *ibid.*, **361**, 235 (1968).

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

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

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

(8) J. G. Converse and R. E. McCarley, *ibid.*, **9**, 1361 (1970).

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

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

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

(12) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964).

(13) P. B. Fleming, J. L. Meyer, W. K. Grindstaff, and R. E. McCarley, *ibid.*, **9**, 1769 (1970).

## Collection and Reduction of Intensity Data

A suitable single crystal of  $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ , about 0.14 mm long and 0.07 mm diameter, was mounted on a glass fiber with its needle axis parallel to the fiber axis. Weissenberg photographs indicated Laue symmetry  $\bar{3}m$  with the trigonal  $c$  axis parallel to the needle axis. No systematic absences were observed. The lattice constants were obtained from Guinier photographs with tungsten as a standard ( $a = 3.15884 \text{ \AA}^{14}$ ) and refined by least-squares methods<sup>15</sup> to the final values  $a = 10.850 \pm 0.005 \text{ \AA}$ ,  $c = 8.615 \pm 0.005 \text{ \AA}$ , and  $V = 878.3 \pm 1.3 \text{ \AA}^3$ . With one formula unit per unit cell the calculated density of  $2.54 \text{ g cm}^{-3}$  agrees well with the observed density of  $2.52 \text{ g cm}^{-3}$ , measured by displacement of  $\text{CCl}_4$ .

Three-dimensional intensity data were collected on an automated Hilger and Watts four-circle diffractometer by a moving-crystal, moving-counter technique. Each reflection was step-scanned from  $\theta(\text{calcd}) - (0.25^\circ + \theta/100)$  to  $\theta(\text{calcd}) + (0.25^\circ + \theta/100)$  at a rate of 0.4096 sec for each step of  $0.01^\circ$ . Stationary background counts were taken at the beginning and at the end of each scan, each for a period equal to half the scan time. Zirconium-filtered Mo  $K\alpha$  radiation was used under a takeoff angle of ca.  $4^\circ$  to measure three complete, symmetry-related sets of data ( $hkl$ ,  $\bar{h}\bar{k}l$ ,  $\bar{h}\bar{k}\bar{l}$ ), each consisting of 621 independent reflections within a sphere of  $2\theta \leq 50^\circ$ . The intensities were measured with a scintillation counter equipped with a pulse height analyzer adjusted to receive 90% of the Mo  $K\alpha$  pulse distribution. The stability of the system, *i.e.*, crystal and electronics, was checked periodically by remeasuring 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.<sup>15</sup> Calculated transmission factors  $A$  varied from 0.81 to 0.85. The linear absorption coefficient for Mo  $K\alpha$  radiation is  $31.95 \text{ cm}^{-1}$ . Errors in the intensities were estimated by  $\sigma(I) = [C_T + C_B + (PI)^2 + (PC_B)^2 + (PC_T)^2]^{1/2}$ , where  $C_T$  is the total count,  $C_B$  is the background count, and  $I$  is  $C_T - C_B$ ;  $P$  was set to 0.05. To obtain  $\sigma(F_o)$  the equation  $\sigma(F_o) = [(I + \sigma(I))/ALp]^{1/2} - |F_o|$  was used.<sup>16</sup>

The structure was actually solved using 491 independent reflections with positive  $h$ ,  $k$ , and  $l$ , and with  $F_o > 3\sigma(F_o)$ . However in the later stages of refinement a new set of data was used where the intensities were averaged over the three symmetry-related sets  $hkl$ ,  $\bar{h}\bar{k}l$ , and  $\bar{h}\bar{k}\bar{l}$ . Standard deviations for the averaged intensities were estimated by

$$\sigma(I_{\text{av}}) = [(C_{T_{\text{av}}} + C_{B_{\text{av}}})/N + (PI_{\text{av}})^2 + (PC_{B_{\text{av}}})^2 + (PC_{T_{\text{av}}})^2]^{1/2}$$

where  $N$  is the number of times a reflection or its equivalent was measured.<sup>17</sup> Finally, 512 averaged  $F_o$  values with  $F_o > 3\sigma(F_o)$  were considered observed.

## Solution and Refinement of Structure

The absence of systematic extinctions and the diffraction symmetry  $\bar{3}m$  had left us with a choice between six possible space groups. A Harker synthesis parallel to (001) revealed the orientation of the  $\text{Nb}_6\text{Cl}_{12}$  unit relative to the lattice and excluded the space groups  $P\bar{3}1m$ ,  $P31m$ , and  $P312$ . To decide between the centrosymmetric  $P\bar{3}m1$  and the noncentrosymmetric  $P3m1$  or  $P321$ , the data sets  $hkl$  and  $\bar{h}\bar{k}l$  were carefully compared. No

(14) "International Tables for X-ray Crystallography," Vol III, Kynoch Press, Birmingham, England, 1962

(15) All computations were performed on the IBM 360/65 computer using the following programs: lattice constant refinement program, a local program written by the authors; the absorption correction program for polyhedral crystals by Busing and Levy, ABCO; intensity data reduction program, a local program by the 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

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

(17) For the reflections 001 and 002 intensities in the three measured sets of data varied considerably but unsystematically. For these two reflections only,  $(C_{T_{\text{av}}} + C_{B_{\text{av}}})/N$  as the statistical part of the error was replaced by  $(\Delta I)^2/N$ , with  $\Delta I$  being the difference between the highest and lowest observation.

systematic discrepancies were detected; hence the space group  $P\bar{3}m1$  was assumed to be correct and this was confirmed later by successful solution of the structure. The rest of the structure was solved by full-matrix, least-squares procedures and by Fourier calculations.<sup>15</sup> Scattering factors for  $\text{Nb}^{2.67+}$  were interpolated from tables given by Thomas and Umeda.<sup>18</sup> Values used for N, C, and H were those given by Hanson, Herman, Lea, and Skillman,<sup>19</sup> while the scattering factor for Cl and anomalous dispersion corrections for Nb and Cl were taken from ref 14. The function minimized in the least-squares refinement was  $\Sigma w(|F_o| - |F_c|)^2$  with  $w = [\sigma(F_o)]^{-2}$ .

Approximate Nb and Cl positions derived from the Harker map and isotropic temperature factors arbitrarily set equal to 1 were used to start the least-squares refinement. Several cycles of refinement of these parameters led to an unweighted  $R$  factor,  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ , of 0.141 and to a weighted  $R$  factor,  $R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$ , of 0.169. A difference Fourier synthesis of the 110 plane revealed the positions of the  $(\text{CH}_3)_4\text{N}^+$  groups, and three cycles of refinement including the C and N parameters lowered  $R_1$  to 0.101 and  $R_2$  to 0.108. A change to anisotropic temperature factors in the form  $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$  followed by two further cycles of refinement resulted in  $R_1 = 0.066$  and  $R_2 = 0.074$ .

At this stage a difference Fourier synthesis revealed the H atoms as maxima varying from 0.5 to  $0.7 \text{ e/\AA}^3$  in positions reasonable for them. These positions, calculated with  $d(\text{C-H}) = 1.09 \text{ \AA}$  and appropriate angular geometry, were now included together with temperature factors arbitrarily set to 3.0. None of the H parameters was refined, but H positions were recalculated after each of the following cycles. Inclusion of the H atoms and two cycles of refinement reduced  $R_1$  to 0.064, and a correction for anomalous dispersion for Nb and Cl plus two further cycles resulted in  $R_1 = 0.059$  and  $R_2 = 0.063$ .

At this point the data set  $hkl$  was replaced by the new set of 512 independent data obtained by averaging the three symmetry-related sets  $hkl$ ,  $\bar{h}\bar{k}l$ , and  $\bar{h}\bar{k}\bar{l}$  as described above. Three cycles of refinement on the averaged data set gave the final values  $R_1 = 0.043$  and  $R_2 = 0.055$ . A final difference electron density map showed two peaks of 1.07 and  $0.85 \text{ e/\AA}^3$  very close to the Nb positions; all other peaks were below  $0.6 \text{ e/\AA}^3$ . Although the thermal parameters for C and N atoms remained positive when converted to anisotropic values, further refinement using anisotropic temperature factors for these atoms showed only slight improvement in the  $R$  factor at the 90% significance level.<sup>20</sup> Therefore it was decided to refine with only isotropic temperature factors for C and N. The shift in the last cycle of isotropic refinement for C and N was less than 0.01 esd. The final standard error for an observation of unit weight was 1.05. A table of observed and calculated structure factors has been deposited,<sup>21</sup> and final positional and thermal parameters are given in Table I.

## Description and Discussion of the Structure

In this structure the  $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$  cluster anions are centered in the eight corners of the trigonal unit cell. Their arrangement parallel to (001) is shown in Figure 1. Equatorial bridging chlorine atoms Cl(1) are situated on the horizontal edges  $a$  and  $b$  and on the short diagonals of the unit cell. Niobium atoms, axial bridging chlorine atoms Cl(2), terminal chlorine atoms Cl(3), and the carbon atoms C(2) occupy special positions on mirror planes at  $30^\circ$  angles to the  $a$  and  $b$  axes. The  $(\text{CH}_3)_4\text{N}^+$  groups are centered on three-fold axes on top of or below three cluster units with each hydrogen atom H(1) of one methyl group reaching into the space between two cluster units. Hydrogen

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

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

(20) W. C. Hamilton, *ibid.*, **18**, 502 (1965).

(21) Table IV, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

TABLE I  
 POSITIONAL AND THERMAL PARAMETERS<sup>a,b</sup> FOR  $[(\text{CH}_3)_4\text{N}]_2\text{Nb}_6\text{Cl}_{18}$ 

Atom	$10^5x$	$10^5y$	$10^5z$	$10^5B_{11}$	$10^5B_{22}$	$10^5B_{33}$	$10^5B_{12}$	$10^5B_{13}$	$10^5B_{23}$
Nb	09270 (5)	-09270 (5)	14306 (9)	771 (11)	771 (11)	452 (13)	433 (10)	-35 (4)	35 (4)
Cl(1)	31398 (23)	0	0	767 (22)	1042 (34)	840 (34)	521 (17)	-5 (13)	-10 (25)
Cl(2)	10361 (13)	-10361 (13)	-32229 (26)	979 (25)	979 (25)	549 (30)	552 (28)	73 (12)	-73 (12)
Cl(3)	20038 (16)	-20038 (16)	30479 (31)	1653 (38)	1653 (38)	1004 (38)	1177 (42)	-195 (16)	195 (16)
Atom	$10^5x$	$10^5y$	$10^5z$	$10^2B$					
N	33333	-33333	-29266 (164)	287 (26)					
C(1)	33333	-33333	-12052 (220)	339 (36)					
C(2)	40915 (61)	-40915 (61)	-34863 (141)	398 (23)					
Atom	$10^4x$	$10^4y$	$10^4z$	$B$					
H(1)	2786	-2786	-0784	3.0					
H(2)	4094	-4094	-4752	3.0					
H(3)	3545	-5185	-3065	3.0					

<sup>a</sup> Numbers in parentheses are the estimated standard deviations in the last significant digits.  $B$  is in  $\text{\AA}^2$  units. <sup>b</sup> Atoms are labeled as in Figure 2.

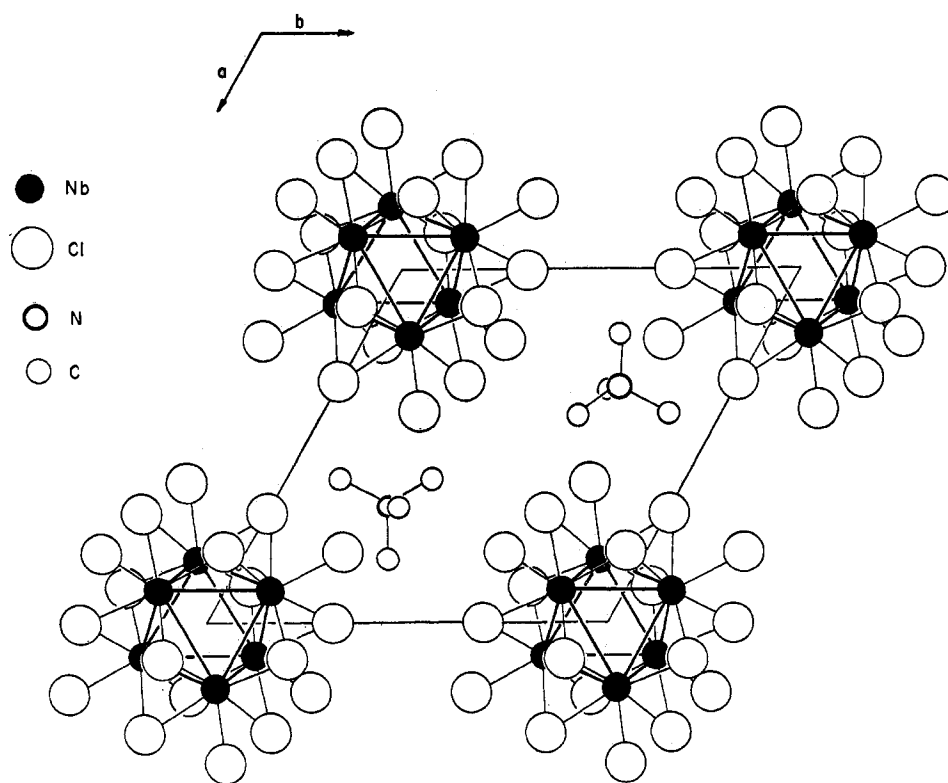


Figure 1.—The crystal packing of  $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$  as seen in the  $[001]$  projection. In this view the  $c$  axis is tilted a few degrees from the direction perpendicular to the plane of the figure.

atoms H(3) (not shown in Figure 1) are the only atoms that occupy a general 12-fold position. The shortest cation-anion contact is that between the methyl group of C(2) and Cl(3), 3.69  $\text{\AA}$ . All other  $\text{C}\cdots\text{Cl}$  contacts are in the range 3.87–4.94  $\text{\AA}$ . Along the  $c$  axis the  $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$  units are stacked on top of each other with the chlorine atoms in approximately a close-packed arrangement.

A single cluster unit is shown in Figure 2 and important interatomic distances and angles are presented in Table II. Though the space group requires only  $D_{3d}$  symmetry, the  $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$  unit is very nearly octahedral. The two sets of Nb-Nb distances are identical within the limits of error, and the  $\text{Nb}_6$  octahedron is practically undistorted. Distances between terminal Cl atoms at the same  $z$  level (Cl(3),1–Cl(3),2) are slightly larger than distances between terminal

Cl atoms on different  $z$  levels (Cl(3),1–Cl(3),6). Thus the octahedron formed by the six terminal chlorine atoms is slightly flattened in the  $c$  direction (along the threefold axis). This slight flattening apparently is caused by the stacking of cluster units and intermolecular Cl-Cl contacts along the  $c$  axis. This stacking interaction also may be responsible for the two different Nb-Cl(bridging) distances, 2.412 and 2.425  $\text{\AA}$ . The axial chlorine atoms Cl(2) are a bit closer to the center of the cluster than the equatorial atoms Cl(1).

Within the tetramethylammonium ions the C-N distances are 1.48 (2) and 1.50 (1)  $\text{\AA}$ . Since these distances are about normal and are of no particular chemical interest in the present structure, no further consideration will be given to them.

Of particular interest in this study were the dimensional changes of the  $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$  anion which result

TABLE II  
INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)  
IN  $[(\text{CH}_3)_4\text{N}]_2\text{Nb}_6\text{Cl}_{18}^{2-}$ <sup>a,b</sup>

Intramolecular interatomic distances		Intramolecular angles	
Nb,1-Nb,2	3.018 (2)	Nb,2-Nb,1-Nb,6	60.01 (2)
Nb,1-Nb,6	3.018 (2)	Nb,5-Nb,1-Nb,6	59.98 (5)
Nb,1-Nb,4	4.268 (2)	Nb,2-Nb,1-Nb,5	90.00 (1)
Nb,1-Cl(1),1	2.425 (2)	Cl(3),2-Cl(3),1-Cl(3),6	59.69 (3)
Nb,1-Cl(2),6	2.412 (2)	Cl(3),5-Cl(3),1-Cl(3),6	60.62 (7)
Nb,1-Cl(3),1	2.457 (3)	Cl(3),2-Cl(3),1-Cl(3),5	90.00 (0)
Cl(1),1-Cl(1),6	3.407 (3)	Nb,4-Nb,1-Cl(3),1	179.27 (24)
Cl(1),1-Cl(2),6	3.408 (3)	Nb,1-Cl(1),1-Nb,6	76.94 (8)
Cl(1),1-Cl(3),1	3.234 (3)	Nb,1-Cl(2),6-Nb,2	77.44 (8)
Cl(2),6-Cl(2),5	3.373 (4)	Cl(1),1-Nb,1-Cl(3),1	82.99 (7)
Cl(2),6-Cl(3),1	3.265 (3)	Cl(2),6-Nb,1-Cl(3),1	84.23 (7)
Cl(3),1-Cl(3),2	6.523 (6)	Cl(1),1-Nb,1-Cl(1),5	89.25 (4)
Cl(3),1-Cl(3),6	6.462 (5)	Cl(2),6-Nb,1-Cl(1),1	89.60 (7)
Cl(3),1-Cl(3),4	9.182 (6)	Cl(2),5-Nb,1-Cl(2),6	88.71 (12)
N-C(1)	1.48 (2)	Cl(2),5-Nb,1-Cl(1),1	161.21 (7)
N-C(2)	1.50 (1)	C(1)-N-C(2)	108.7 (7)
		C(2)-N-C(2)	110.2 (5)

Intermolecular distances  
(adjacent anions)

Cl(1)-Cl(1)	4.037 (3)
Cl(2)-Cl(2)	3.629 (5)
Cl(2)-Cl(3)	3.692 (4)

<sup>a</sup> Numbers in parentheses are the estimated standard deviations in the last significant digits. <sup>b</sup> Atoms are labeled as in Figure 2.

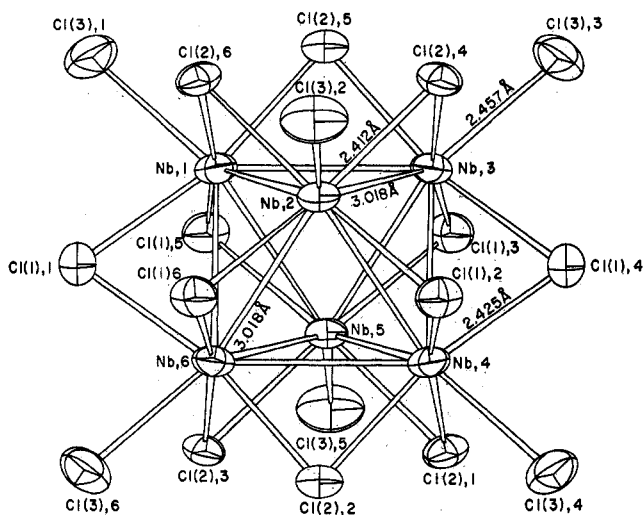


Figure 2.—The structure of the cluster anion  $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{2-}$  showing the atom-labeling scheme.

from a change in the oxidation state of the anion. These changes, as indicated above, are important for the verification of the basic ideas about bonding in the  $\text{M}_6\text{X}_{12}^{n+}$  cluster units and also provide useful information which should be of value in the interpretation of both electronic and vibrational spectroscopic data. The structural data for  $\text{K}_4\text{Nb}_6\text{Cl}_{18}$  previously determined by Simon, Schnering, and Schäfer<sup>4</sup> may be compared with the data given here for  $[(\text{CH}_3)_4\text{N}]_2[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]$ . Thus, in these two salts which contain the same cluster units differing only in oxidation state, the effects of removing two electrons on passing from  $\text{Nb}_6\text{Cl}_{18}^{4-}$  to  $\text{Nb}_6\text{Cl}_{18}^{2-}$  are readily discerned.

As shown by the data given in Table III the most obvious changes are in the Nb-Nb and Nb-Cl bond distances. Removal of two electrons causes an increase of 0.10 Å in the Nb-Nb bond distance without any significant departure from  $O_h$  symmetry for the cluster of six metal atoms. This result is very good evidence that the two electrons in question reside in

TABLE III  
AVERAGE INTERATOMIC DISTANCES AND ANGLES IN  
 $\text{M}_6\text{Cl}_{18}^{n-}$  COMPOUNDS<sup>a</sup>

	$\text{K}_4\text{Nb}_6\text{Cl}_{18}^{4-}$ <sup>b</sup>	$[(\text{CH}_3)_4\text{N}]_2\text{Nb}_6\text{Cl}_{18}^{2-}$	$\text{H}_2\text{Ta}_6\text{Cl}_{18} \cdot 6\text{H}_2\text{O}^c$
$d(\text{M}-\text{M})$	2.92	3.02	2.96
$d(\text{M}-\text{Cl}_b)^d$	2.48	2.42	2.41
$d(\text{M}-\text{Cl}_t)^e$	2.60	2.46	2.51
$d(\text{Cl}_b-\text{Cl}_b)$	3.46	3.40	3.38
$d(\text{Cl}_b-\text{Cl}_t)$	3.31	3.25	3.25
$d(\text{center}-\text{M})^f$	2.06	2.13	2.09
$d(\text{center}-\text{Cl}_b)^f$	3.46	3.40	3.38
$d(\text{center}-\text{Cl}_t)^f$	4.67	4.59	4.60
$d(\text{Cl}_b \text{ plane}-\text{M})^g$	0.39	0.27	...
$\text{M}-\text{Cl}_b-\text{M}$	71.9	77.2	...
$\text{Cl}_b-\text{M}-\text{Cl}_b$	88.6	89.3	...
$\text{Cl}_b-\text{M}-\text{Cl}_t$	81.0	83.6	...

<sup>a</sup> All distances listed in ångströms; all angles in degrees. <sup>b</sup> Values computed from data given in ref 4. <sup>c</sup> Values computed from data given by C. B. Thaxton and R. A. Jacobson, *Inorg. Chem.*, **10**, 1460 (1971). <sup>d</sup>  $\text{Cl}_b$  indicates bridging chlorine. <sup>e</sup>  $\text{Cl}_t$  indicates terminal chlorine. <sup>f</sup> Distance from center of cluster to indicated atom. <sup>g</sup> Distance from metal atom to plane formed by four nearest bridging Cl atoms.

bonding orbitals, as predicted by the previous MO treatment.<sup>12</sup> Because  $(\text{Nb}_6\text{Cl}_{12})^{2+}$  as well as  $(\text{Nb}_6\text{Cl}_{12})^{4+}$  units have been shown to be diamagnetic,<sup>8</sup> it is evident that both electrons which can be removed are paired in the same orbital. This orbital has either  $a_{1g}$  or  $a_{2u}$  symmetry.<sup>12</sup> When comparing these Nb-Nb bond distances it is important that the cluster units be the same. For example changing the halogen in the cluster unit may make a significant difference in the Nb-Nb distance; compare the values 2.80, 2.92, and 2.97 Å in  $\text{Nb}_6\text{F}_{15}$ ,<sup>22</sup>  $\text{K}_4\text{Nb}_6\text{Cl}_{18}$ ,<sup>4</sup> and  $[(\text{CH}_3)_4\text{N}]_3\text{Nb}_6\text{Cl}_{18}$ ,<sup>23</sup> respectively.

As expected oxidation of the cluster unit results in a decrease of the Nb-Cl bond distances. The twelve bridging chlorine atoms move in closer to the center of the cluster by 0.06 Å, which also is just the decrease in the Nb-Cl(bridging) bond distance resulting from the two-electron oxidation. However the change in the Nb-Cl(terminal) bond distance is most profound. This distance is shorter by 0.14 Å (average) in the oxidized species. In both  $\text{Nb}_6\text{Cl}_{18}^{4-}$  and  $\text{Nb}_6\text{Cl}_{18}^{2-}$  the bond to the terminal chlorine atoms appears to be longer than a normal covalent bond (ca. 2.35-2.40 Å). Very likely the relatively long bond here is determined by the unfavorable geometry of the clusters. In each case the metal atoms are located in positions displaced from the center of the plane of the four nearest bridging chlorine atoms toward the interior of the cluster. Hence nonbonded repulsion between the terminal and adjacent bridging chlorine atoms prevents closer approach of the terminal chlorines to the niobium atoms. In line with this argument we note that the nonbonded Cl(bridging)-Cl(terminal) distances are unusually small (3.25-3.31 Å).

A second manifestation of the weakened metal-metal bonding in the oxidized species is noticed in the smaller distance of the metal atoms from the center of the plane of surrounding bridging chlorine atoms and the larger Nb- $\text{Cl}_b$ -Nb bond angles. The whole effect resulting from removal of two electrons and passing from the 4- to the 2- species is illustrated

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

(23) F. W. Koknat and R. E. McCarley, submitted for publication.

best by comparing the atom positions relative to the center of the cluster unit. Stated simply the octahedron of metal atoms is expanded and the surrounding cluster of chlorine atoms, both bridging and terminal, is contracted as a result of this process. Consequently, the Nb-Cl(terminal) bond is shortened most because the Nb and Cl atoms move directly toward each other.

If local coordinates on the metal atoms are chosen so that the  $z$  axes point toward the center of the octahedron, then the metal MO's most strongly affected by the removal of electrons are those constructed from the  $d_{2z}$  set, *viz.*,  $a_{1g}$ ,  $e_g^*$ , and  $t_{2g}^*$ .<sup>12</sup> Of this set only  $a_{1g}$  is bonding and occupied with electrons in the  $Nb_6Cl_{18}^{4-}$  cluster. From the dimensional changes discussed above it appears that the  $d_{2z}$  orbitals may be extracted from metal-metal bonding upon oxidation and used for tighter binding of the terminal Cl atoms. Thus a comparison of the structural data for  $Nb_6Cl_{18}^{n-}$

species suggests that  $a_{1g}$  is in all cases the bonding MO of highest energy or that the  $a_{1g}$  and  $a_{2u}$  levels cross over with successive removal of electrons in the oxidation process.

Also included in Table III are structural data for  $Ta_6Cl_{18}^{2-}$  as recently determined from a study of  $H_2Ta_6Cl_{18} \cdot 6H_2O$ .<sup>24</sup> The most noteworthy features of these data are the Ta-Ta distance which is 0.06 Å shorter and the Ta-Cl(terminal) distance which is 0.05 Å longer than the corresponding distances in the isoelectronic  $Nb_6Cl_{18}^{2-}$ . Since the M-Cl(bridging) distances are nearly equivalent, the principal difference appears to be stronger metal-metal bonding and weaker M-Cl(terminal) bonding in the tantalum cluster compared to the niobium cluster. Chemical evidence<sup>2</sup> does suggest that the tantalum clusters are more stable toward degradation than their niobium counterparts.

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

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF WATERLOO, WATERLOO, ONTARIO, CANADA, AND UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

## The Crystal and Molecular Structure of the Five-Coordinated Copper(II) Complex with *N*- $\beta$ -Dimethylaminoethylsalicylaldimine

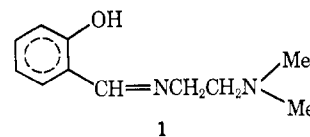
By P. C. CHIEH AND GUS J. PALENIK\*

Received March 31, 1971

The green compound bis(*N*- $\beta$ -dimethylaminoethylsalicylaldiminato)copper(II),  $Cu[OC_6H_4CHNCH_2CH_2N(CH_3)_2]_2$ , crystallizes as monoclinic plates with  $a = 13.079$  (5),  $b = 11.816$  (11),  $c = 15.071$  (8) Å, and  $\beta = 102.52$  (6)°. The space group is  $P2_1/n$  with four molecules per unit cell,  $d_m = 1.295$  (5) g/cm<sup>3</sup>, and  $d_c = 1.302$  (2) g/cm<sup>3</sup>. Diffractometer data were measured using Cu K $\alpha$  radiation and the structure has been refined by least-squares methods with anisotropic thermal parameters to a final  $R$  of 0.048 for 3081 observed reflections. The crystal consists of discrete molecules of the complex with the copper atom surrounded by five of the six possible donor atoms; the  $\beta$  nitrogen of one ligand is uncoordinated. The molecule is severely distorted but appears to be closer to a trigonal-bipyramidal rather than a square-pyramidal configuration. Some pertinent distances are Cu to O of 1.930 (3) and 1.943 (3) Å, Cu to the azomethine nitrogens of 1.944 (3) and 1.948 (3) Å, and Cu to a dimethylamino nitrogen of 2.553 (4) Å. The long Cu to N distance is in the equatorial plane in the trigonal-bipyramidal configuration which is rather unusual for five-coordinated copper compounds with this configuration.

### Introduction

A Cu(II) ion in a regular octahedral field is unstable<sup>1</sup> and is expected to distort to remove the degeneracy of the  $e_g$  orbitals. The result is either a compressed or elongated octahedron with the latter being far more common. The final distribution of electrons is unsymmetrical, producing changes in the molecular dimensions of symmetrical chelating ligands.<sup>2,3</sup> Whether the final configuration (the elongated or compressed octahedron) is a function of the type of ligand atoms is an intriguing question. During our study of Cu(II) and high-spin Mn(III) complexes which are susceptible to these distortions, we prepared the bis(*N*- $\beta$ -dimethylaminoethylsalicylaldiminato)copper(II) complex. The ligand, **1**, is a potential anionic tridentate ligand; we hoped the copper(II) complex would be octahedral. The results of our crystal structure analysis have



revealed that the Cu(II) ion is pentacoordinated with one of the dimethylamino groups not bonded to the Cu(II) ion. The resulting configuration is severely distorted from either idealized pentacoordinated configuration and contains several unusual features not observed in other copper complexes.<sup>4</sup>

### Experimental Section

Bis(*N*- $\beta$ -dimethylaminoethylsalicylaldiminato)copper(II) crystallizes from cyclohexane as green plates elongated along  $b$  with (001) well developed. Weissenberg, precession, and rotation photographs were taken to obtain preliminary cell constants and to determine the space group. A second crystal with dimensions of  $0.16 \times 0.18 \times 0.16$  mm (along  $a$ ,  $b$ ,  $c$ , respectively) was used for the intensity measurements and for obtaining refined cell

\* Address correspondence to this author at the University of Florida.

(1) H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser. A*, **161**, 220 (1937).

(2) M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Amer. Chem. Soc.*, **91**, 1859 (1969).

(3) M. Mathew and G. J. Palenik, *J. Coord. Chem.*, in press.

(4) A preliminary account of this study was presented at the American Crystallographic Association Meeting, Ottawa, Ontario, Canada, Aug 1970.