Chemistry of the Polynuclear Metal Halides. X. Nuclear Quadrupole Resonance Study of Bis(tetramethylammonium) Hexachlorododeca-μ-chloro-hexaniobate[1]

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The room-temperature ^{93}Nb, ^{35}Cl, and ^{37}Cl nuclear quadrupole resonance spectra of $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$ have been recorded. Temperature-dependent studies of both the nqr and the X-ray powder diffraction pattern indicate that the crystals undergo a reversible transformation which apparently quenches disorder into the structure at lower temperatures. An approximate population analysis for electrons in the $Nb_6Cl_{12}^{4+}$ cluster yields 14 electrons available for metal–metal bonding as predicted by theory. A wide line induction spectrometer permitting easy and highly precise frequency measurement of nqr frequencies is also described.

Introduction

To date nuclear quadrupole resonance (nqr) data for only three compounds containing the basic cluster unit $M_6X_{12}^{n+}$ have been reported.[2] An especially interesting derivative of this type is $Nb_6Cl_{12}^{4+}$ because nqr signals of both Nb and Cl can be observed. Furthermore, since ^{93}Nb has a nuclear spin (I) of $^9/_2$, both the asymmetry parameter, η, and the quadrupole coupling constant, e^2Qq, can be determined directly from the four observable ^{93}Nb resonances. Because of the ability, in principle at least, to relate nqr frequencies to bonding parameters, a study of a cluster unit in which both metal and halogen resonances can be observed should aid in our understanding of the bonding in hexanuclear metal cluster compounds.

Experimental Section

The sample of $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$, generously provided by Dr. F. W. Koknat, was prepared according to published methods.[3]

Resonances were initially observed using a Wilks NQR-1A superregenerative nuclear quadrupole resonance spectrometer. Approximate frequency measurements of the strongest band of the observed spectrum were made using spectrum-analyzing techniques.[4] A modified coil shield was fabricated from copper and covered with Pyrex wool which permitted the passage of cold nitrogen gas (boiled from a liquid nitrogen dewar) through the sample compartment of the Wilks spectrometer. Temperatures were monitored using a Rubicon portable precision potentiometer and a copper–constantan thermocouple.

Precise frequency determinations were accomplished using continuous-wave nuclear induction. The validity of the use of nuclear induction techniques with magnetic field modulation for nqr detection has been discussed by Smith.[5] A wide-line induction spectrometer described elsewhere[6] employing Varian Associates V4230B wide-line induction probes with magnetic field modulation was used to perform continuous averaging[7] of the nqr spectra. A modified 400-channel analyzer[8] was used in the process of continuous averaging. A block diagram of the continuous-wave system is presented in Figure 1. Frequency scanning of the Marconi TF2022 voltage-controlled radiofrequency signal generator was accomplished through the ap-

propriate amplification and offset of the analog channel address or ramp voltage of the multichannel analyzer. The interval of frequency scanned was usually less than 100 kHz and, thus, sufficiently narrow to avoid the necessity of retuning the transmitter output and receiver input[6] circuits during the scan. Rebalancing of the induction probe was not required within the intervals scanned. Resonance frequencies were read directly from a Hewlett-Packard Model 5245L frequency counter. Signal averaging over periods of 1.5–24 hr was necessary, particularly for the weak ^{37}Cl resonances.

Variable-temperature X-ray powder diffraction patterns were obtained using a Materials Research Corp. Model X-86NC diffractometer attachment with a Philips diffractometer employing Cu Kα radiation. The (111) and (333) reflections of a silicon single crystal were used as internal reference points.

Results and Discussion

The experimental results are listed in Table I. Relevant structural information is listed in Table II, and a single cluster unit is shown in Figure 2.

TABLE I
NQR FREQUENCIES IN $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$

Nucleus	Transition	ν_Q, MHz Exptl[a,b]	ν_Q, MHz Calcd[c]	Comments
^{93}Nb	$\pm^1/_2 \rightarrow \pm^3/_2$	5.563	5.565	
^{93}Nb	$\pm^3/_2 \rightarrow \pm^5/_2$	11.122	11.122	
^{93}Nb	$\pm^5/_2 \rightarrow \pm^7/_2$	16.685	16.685	
^{93}Nb	$\pm^7/_2 \rightarrow \pm^9/_2$	22.249	22.247	
^{35}Cl	$\pm^1/_2 \rightarrow \pm^3/_2$	12.556		Bridging Cl
^{37}Cl	$\pm^1/_2 \rightarrow \pm^3/_2$	9.897		Bridging Cl

[a] Frequencies ± 1.0 kHz. [b] Temperature 23°. [c] Using $e^2Qq = 133.48$ MHz and $\eta = 0.008$.

TABLE II
X-RAY STRUCTURAL DATA—AVERAGE DISTANCES AND ANGLES[a]

Compd	$M-Cl_b$	$M-Cl_t$	$M-Cl_b-M$
$[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$[b]	2.42	2.46	77.2
Nb_2Cl_{10}[c]	2.56	2.25	101.3

[a] All distances listed in ångströms; angles in degrees. [b] Reference 3. [c] D. E. Sands, A. Zalkin, and R. E. Elson, *Acta Crystallogr.*, 12, 21 (1959).

These results are not completely satisfactory because of the lack of observed resonances assignable to the terminal Cl atoms. Repeated searches from 3 to 33 MHz yielded only the listed results. In group III trihalides terminal halogen atom resonances are at higher frequencies than bridging halogen atom resonances,[9] which is consistent with the greater bond distance of the bridging halogens. However in the cluster anions the

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 3121.

(2) W. van Bronswyk and R. Nyholm, *J. Chem. Soc. A*, 2084 (1968).

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(4) G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instrum.*, 37, 1081 (1966).

(5) G. W. Smith, *Phys. Rev.*, 149, 346 (1966).

(6) D. R. Torgeson, *Rev. Sci. Instrum.*, 38, 612 (1967).

(7) M. P. Klein and G. W. Barton, Jr., *ibid.*, 34, 754 (1963).

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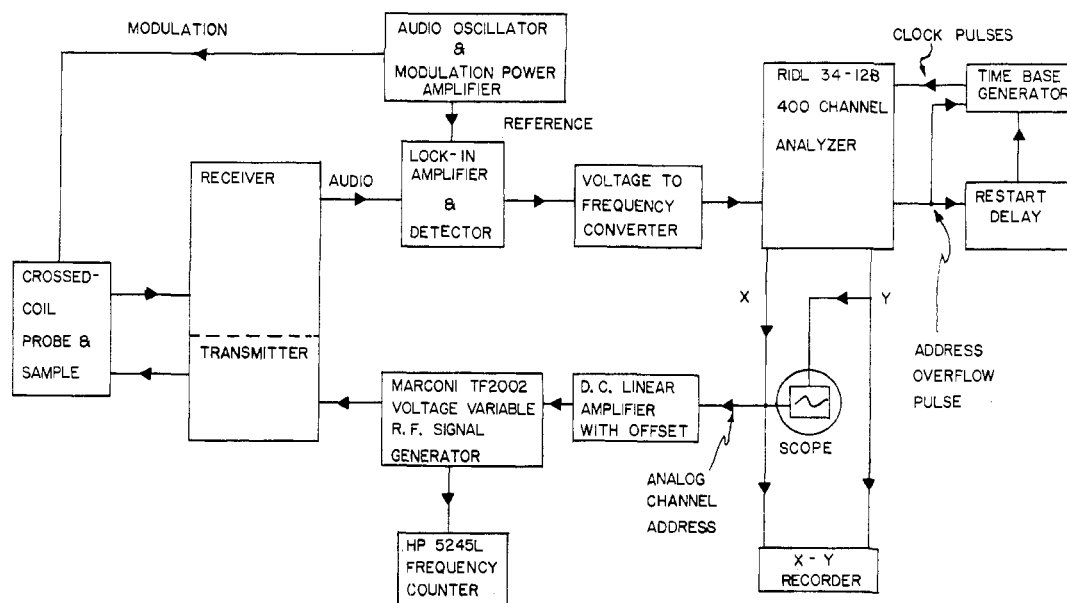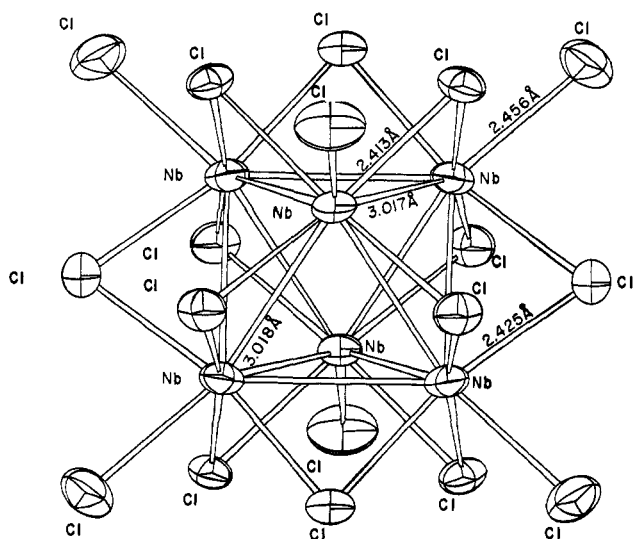(9) G. E. Peterson and P. M. Bridenbaugh, *J. Chem. Phys.*, 51, 238 (1969).

Figure 1.—Block diagram of the wide-line induction spectrometer.

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

Nb–Cl terminal bond distances are significantly longer than the Nb–Cl bridging distances[3] (see Table II). Weaker covalent binding of these terminal halogens also is suggested by the ability of other donor atoms to substitute into the terminal positions under mild conditions while under the same conditions there is no evidence for substitution into the bridging positions.[10] Thus, based on both the structural and chemical differences, we believe that in the cluster anions the terminal halogens are rather ionic in nature and that the resonance frequency for them is lower than the resonance frequency for the bridging halogens.

Low-temperature sweeps were made in an attempt to observe the missing signals. Observation of the expected increase in resonance frequency with reduced temperature was not as interesting as the attendant decrease, rather than the expected increase, in the signal-to-noise ratio of the resonances. At 230°K, the ^{35}Cl signal was not detected and the ^{93}Nb $\pm^3/_2 \rightarrow \pm^5/_2$

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

transition was only barely detectable. Van Bronswyk and Nyholm[2] have also reported that no signals in the Pt_6Cl_{12} or Pd_6Cl_{12} clusters were observed at liquid nitrogen temperature. Similarly, rather than sharpening at reduced temperatures, certain lines in the X-ray diffraction patterns also broadened and lost intensity indicative of some type of minor, reversible structural variation in the crystals between room and liquid nitrogen temperature. Possibly this effect is associated with the freezing of the methyl hydrogen atoms into disordered positions.

The Cl resonances observed are assigned as belonging to bridging Cl atoms on the basis of their proximity in frequency to bridging ^{35}Cl atoms in Nb_2Cl_{10},[11] 13.06 MHz, and Ta_2Cl_{10},[12] 13.37 MHz (mean of triplet). The reasonableness of this assignment is revealed after numerical interpretation following the suggestions of Lucken.[13] If the coordinate system in Figure 3 is
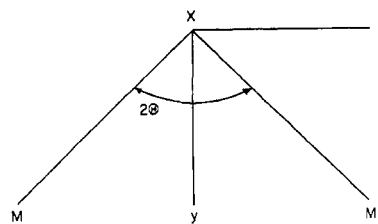
Figure 3.—Coordinate system for bridging halogen atoms. The z axis is perpendicular to the M–X–M plane.

chosen, where 2θ is the M–X–M bond angle or the angle between the hybrid halogen orbitals bonding the halogen to the metal, the following hybrid orbital wave functions may be written for the case of the M_2X_{10} molecules

$$\phi_1 = \psi_{p_z}$$

$$\phi_2 = \psi_s \cot \theta + \psi_{p_y}(1 - \cot^2 \theta)^{1/2}$$

(11) A. H. Reddoch, Ph.D. Thesis, University of California, Berkeley, Calif., 1959; AEC Report UCRL-8972, and references contained therein.

(12) I. Safin, B. Pavlov, and D. Shtern, *Zavod. Lab.*, **30**, 676 (1964).

(13) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York, N. Y., 1969, p 265.

$$\phi_3 = \frac{1}{\sqrt{2}}[\psi_s(1 - \cot^2\theta)^{1/2} + \psi_{p_x} - \psi_{p_y}\cot\theta]$$

$$\phi_4 = \frac{1}{\sqrt{2}}[\psi_s(1 - \cot^2\theta)^{1/2} - \psi_{p_x} - \psi_{p_y}\cot\theta]$$

The population of ϕ_1 and ϕ_2 (N^1 and N^2, respectively) was assumed to be 2, while the population of ϕ_3 and ϕ_4 (N^3 and N^4, respectively) was defined as a. Three other relations are known to be valid[13,14]

$$\nu_Q(I = {}^3/_2) = (e^2Qq/2h)[1 + (\eta^2/3)]^{1/2}$$
$$\eta = -3\cos 2\theta$$
$$(e^2Qq_{mol}/e^2Qq_{atm})[1 + (\eta/3)] = 2 - a$$

In the case of the $Nb_6Cl_{12}^{4+}$ cluster it was necessary to invoke "bent" bonds by assuming $2\theta = 90°$ to interpret the results because no possible sp hybridization of the bridging Cl orbitals can account for the observed Nb–Cl–Nb angle of 77.2°. We have interpreted Reddoch's results[11] taking into account the Nb–Cl–Nb angle of 101.3° for the bridging Cl atoms of Nb_2Cl_{10}. The population of the ith atomic orbital (N_i) can be determined from[15]

$$N_i = \sum_k N^k |C_i^k|^2$$

where C_i^k is the coefficient of the ith atomic orbital in the kth hybrid orbital, and N^k is the population of the kth hybrid orbital. Townes and Schawlow's value[16] of $e^2Qq = -109.7$ MHz for ^{35}Cl was used to obtain the results shown in Table III. Of 8 possible electrons on

TABLE III
NUMERICAL RESULTS

	η	e^2Qq, MHz	a	N_s	N_{p_x}	N_{p_y}
[(CH₃)₄N]₂[(Nb₆Cl₁₂)Cl₆]	0.0	25.112	1.77	2.00	1.77	1.77
Nb₂Cl₁₀	0.588	24.731	1.73	1.91	1.73	1.82

each bridging chlorine atom, 7.54 in $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$ and 7.46 in Nb_2Cl_{10} were accounted for in this manner.

Two qualitative comments concerning the ^{93}Nb molecular coupling constant can be made. First, the small asymmetry parameter for the ^{93}Nb nucleus does not appear inconsistent with the cylindrical symmetry about any $Nb-Cl_t$ bond axis as revealed by the X-ray structural determination. Second, the experimental value for the quadrupole coupling constant is, to the authors' knowledge, the largest reported to date for ^{93}Nb.

Ideally, one would like to compare a calculated value for the molecular field gradient, eq_{zz}, with the experimentally determined value, -9.21×10^{15} esu/cm³ (based on a value of -0.20 barn[17] for the quadrupole moment, eQ, of ^{93}Nb). It is possible to write eq_{zz} as a function of the population of the orbitals on Nb involved in bonding and the $\langle r^{-3}(nl)\rangle$ of the respective orbitals[18]

$$eq_{zz} = eq_{420}[N_{d_{z^2}} + {}^1/_2(N_{d_{zx}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})] + eq_{510}[N_{p_z} - {}^1/_2(N_{p_x} + N_{p_y})]$$

where[16]

$$eq_{n10} = \frac{2l(l+1)e}{(2l-1)(2l+3)}\langle 1/r^3(nll)\rangle$$

However, this does not appear possible at the present time. In the absence of any calculations for $\langle r^{-3}(51)\rangle$, any approximate value of eq_{510} would be highly speculative. The lack of information about the resonance frequencies of the terminal halogens further complicates the matter. Calculations of the type carried out by Cotton and Haas[19] and by Robin and Kuebler[20] do not appear germane because they do not adequately consider the role of the bridging and terminal halogens in the bonding. Clearly, the molecular coupling constant of the ^{93}Nb is sensitive to the nature of the interaction between the niobium and both types of halogen atoms. Even if more complete calculations were available, the unreliability of a Sternheimer shielding factor (R), probably necessary for ^{93}Nb, would jeopardize the results.

If it is assumed that the nuclear quadrupole resonance of the terminal Cl atoms was not observed because the frequency was outside the range of our spectrometer, *i.e.*, <3 MHz, then the Nb–Cl$_t$ bonds can be assessed as highly ionic. In order for the frequency to be <3 MHz these bonds would have to be *ca.* 90% ionic; and since there is no reason to believe π bonding is at all significant, the frequency should not be lowered owing to π bonding. On this basis an approximate population analysis for electrons in the cluster can be made.

Twelve bridging chlorine atoms, each with a charge of -0.54, as indicated by the nqr data, and six terminal chlorine atoms, each with a charge of -0.9, assuming an ionic character of *ca.* 90%, account for a total charge of -11.88 on the chlorine atoms. Subtracting 2 from -11.88 to account for the -2 charge on the cluster ion, a value of *ca.* $+10$ (9.88) for the net charge of the Nb_6 cluster is obtained. Of the 30 total valence electrons available on the 6 Nb atoms, 20 electrons are left on the Nb_6 cluster. These 20 electrons can be divided into those involved in bonding to bridging chlorine atoms, those involved in bonding to terminal chlorine atoms, and those involved in metal–metal bonding. There are 5.52 electrons involved in the 24 bonds to bridging chlorine atoms, or 0.23 electron is involved in each bond. Additionally, 0.6 electron is involved in the 6 bonds to terminal chlorine atoms; *i.e.*, 0.1 electron is involved in each bond. Of the 20 electrons available for bonding in the Nb_6 cluster *ca.* 6 are involved in Nb–Cl bonds leaving 14 electrons available for metal–metal bonding. This is in agreement with theory[19] which predicts 14 electrons involved in metal–metal bonding in one of two possible configurations: $[t_{1u}t_{2g}a_{2u}]^{14}$ or $[t_{1u}t_{2g}a_{1g}]^{14}$.

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