Inorganic Chemistry, Vol. 12, No. 9, 1973 **1967**

Contribution from the Department of Chemistry,
University of Western Ontario, London 72, Canada

Niobium-93 Nuclear Magnetic Resonance Study of Hexahaloniobates and Pentahaloniobium-Acetonitrile Adducts

R. G. KIDD* and H. G. SPINNEY

Received July 19, 1972

The seven hexahaloniobate anions in the series $[NbCl_nBr_{6-n}]^-$ have been prepared in MeCN solution and their niobium-93 nmr spectra have shown that for $[NbCl_2Br_4]^-$, $[NbCl_3Br_3]^-$, and $[NbCl_4Br_2]^-$, only the cis isomers are present in solution. The six pentahaloniobium–acetonitrile adducts in the series $NbCl_nBr_{5-n}\cdot MeCN$ have been prepared in MeCN and in CH_2Cl_2 solution and only seven of the twelve possible geometric isomers are found to be present. The pairwise additivity model for predicting chemical shifts has been extended from four-coordinate to six-coordinate complexes where it constitutes a powerful technique for identifying in solution the presence of specific geometric isomers. Chlorine substitution causes an *upfield* shift of the niobium-93 resonance relative to bromine substitution.

Introduction

The state of $NbCl_5$ and $NbBr_5$ in acetonitrile solution has long been a topic of controversy. It is generally accepted that they exist as pseudooctahedral halogen-bridged dimers in the solid state.[1,2] Kepert and Nyholm found that $NbCl_5$ exists as a 1:1 acetonitrile adduct in acetonitrile.[3] Later workers, however, interpreted the charge-transfer spectra of $NbCl_5$ in acetonitrile as that of the chlorine-bridged dimer.[4] Recently, an intensive vibrational study of $NbX_5\cdot NCCY_3$ (X = Cl or Br; Y = H or D) in the solid state and in acetonitrile solution by Ozin and Walton[5] leaves little doubt that these species are six-coordinate, molecular, and monomeric.

The $NbCl_6^-$ and $NbBr_6^-$ ions have also been prepared and are well characterized,[4,6-8] generally as the tetraalkylammonium salts prepared from the appropriate thionyl halide. In addition, the ions $[NbX_5Y]^-$ (X = Cl or Br; Y = Cl, Br, or I) have been prepared and characterized as the tetraethylammonium salts.[9] Compounds of the type $Et_4N[NbX_4Y_2]$ could not, however, be isolated.[9]

Much of the controversy associated with the nature of niobium(V) halides in solution has arisen because of the difficulty in characterizing the species present, coupled with their propensity for hydrolysis. We now wish to report an improved method for characterizing niobium(V) halides in solution based upon their ^{93}Nb nmr spectra. Comprehensive studies of both the $[NbCl_nBr_{6-n}]^-$ system $(0 \leqslant n \leqslant 6)$ and the $NbCl_nBr_{5-n}\cdot MeCN$ system $(0 \leqslant n \leqslant 5)$ are here reported in which all possible stoichiometries in each system have been prepared and the natures of the geometric isomers present are characterized. A controlled-hydrolysis experiment has been carried out which clarifies the relationship between the $[NbCl_nBr_{6-n}]^-$-MeCN system and the $NbCl_nBr_{5-n}\cdot MeCN$ system. By using the ^{93}Nb spectral data obtained in this study, we have extended the pairwise additivity model developed by Vladimiroff and Malinowski[10] from the four-coordinate to the six-coordinate case where its applicability is sufficiently good to enable one to distinguish unambiguously cis from trans geometric isomers.

Pairwise Additivity Model

In attempting to provide a theoretical interpretation for the composition dependence of any physical property of a molecule, the first-order approach to the problem is generally to try to evaluate substituent constants which can be summed to yield a calculated value for the desired property. Examples of this approach are the use of Pascal constants in the prediction of diamagnetic susceptibilities and the use of Hammett σ parameters in predicting the dissociation constants of substituted benzoic acids. Only if this approach proves to be inadequate, as it does in the present instance, is one forced to use a more sophisticated second-order approach which recognizes the influence of one substituent upon another. Chemical shifts for ^{93}Nb calculated using this first-order approach are given in Tables I and II in the last column and obtained for the complex $[NbCl_nBr_{6-n}]^-$ using the relationship

$$\delta_{\text{calcd}} = \frac{n}{6}\delta_{NbCl_6^-} + \frac{6-n}{6}\delta_{NbBr_6^-}$$

A second-order approach which has met with success on a broad front in rationalizing and predicting the chemical shifts of a variety of nuclei is the pairwise additivity model introduced by Vladimiroff and Malinowski.[10] By recognizing the change caused by one substituent in the wave function for all neighboring substituents, this model allows one to calculate the chemical shift for a central atom by the summing of pairwise interaction parameters for all substituents taken as adjacent pairs. This model has already been used successfully to rationalize the chemical shifts of boron-11,[11] carbon-13,[11] aluminum-27,[12] and germanium-73[13] in four-coordinate tetrahedral environments. In these instances, the chemical shift of the central atom M in the tetrahedral compound is calculated by summing the six pairwise interaction parameters corresponding to the six edges of the tetrahedron. A first-order treatment of these tetrahedral compounds would involve summing only the four substituent constants for the ligands.

The present study constitutes the first application of the pairwise additivity model to the chemical shift data from a six-coordinate system. *The importance of establishing that the model can indeed be extended to the six-coordinate case*

---

(1) A. Zalkin and D. E. Sands, *Acta Crystallogr.*, **11**, 615 (1958).

(2) I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc. A*, 2765 (1968).

(3) D. L. Kepert and R. S. Nyholm, *J. Chem. Soc.*, 2871 (1965).

(4) C. Furlani and E. Zinato, *Z. Anorg. Allg. Chem.*, **351**, 210 (1967).

(5) G. A. Ozin and R. A. Walton, *J. Chem. Soc. A*, 2236 (1970).

(6) D. M. Adams, J. Chatt, J. M. Davidson, and J. Geratt, *J. Chem. Soc.*, 2189 (1963).

(7) K. W. Bagnall and D. Brown, *J. Chem. Soc.*, 3021 (1964).

(8) G. A. Ozin, *J. Chem. Soc. A*, 2765 (1968).

(9) G. A. Ozin, G. W. A. Fowles, D. J. Tidmarsh, and R. A. Walton, *J. Chem. Soc. A*, 642 (1969).

(10) T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, **46**, 1830 (1967).

(11) B. F. Spielvogel and J. M. Purser, *J. Amer. Chem. Soc.*, **93**, 4418 (1971).

(12) E. R. Malinowski, *J. Amer. Chem. Soc.*, **91**, 4701 (1969).

(13) R. G. Kidd and H. G. Spinney, *J. Amer. Chem. Soc.*, **95**, 88 (1973).

Table I. ^{93}Nb Shifts for the $[NbCl_nBr_{6-n}]^-$ System in MeCN

	Additivity coeff			ppm		
Species	Cl-Cl	Cl-Br	Br-Br	δ_{calcd} $\Sigma c_{i-j}\eta_{i-j}$[a]	δ_{obsd}[b]	δ_{calcd} first order
$NbCl_6^-$	12	0	0	0	0	0
$NbCl_5Br^-$	8	4	0	−131	−132	−122
$NbCl_4Br_2^-$						
Cis	5	6	1	−258	−258	−244
Trans	4	8	0	−263		
$NbCl_3Br_3^-$						
Cis	3	6	3	−380	−380	−366
Trans	2	8	2	−384		
$NbCl_2Br_4^-$						
Cis	1	6	5	−502	−501	−487
Trans	0	8	4	−506		
$NbClBr_5^-$	0	4	8	−619	−621	−609
$NbBr_6^-$	0	0	12	−731	−731	−731

[a] Additivity parameters values (ppm): $\eta_{Cl-Cl} = 0$; $\eta_{Cl-Br} = -32.82$; $\eta_{Br-Br} = -60.94$. [b] Error limits on observed chemical shifts are ±2 ppm. It is illuminating to note that successive substitution of Br for Cl causes a *downfield* shift. This anomalous shift direction has also been observed in the halogen dependence of ^{47,49}Ti shifts: R. G. Kidd and H. G. Spinney, *J. Amer. Chem. Soc.*, 94, 6686 (1972).

lies in the fact that it provides an unambiguous method for identifying specific geometric isomers of six-coordinate complexes. Had the chemical shift of the central atom M in such a complex been a first-order function of the ligand coordination only, this identification would not have been possible.

The pairwise additivity model applied to the generalized six-coordinate complex is best visualized in terms of a ligand redistribution reaction occurring between MX_6 and MY_6 to give all seven redistribution products having stoichiometries MX_nY_{6-n} $(0 \leqslant n \leqslant 6)$. Because each of the MX_2Y_4, MX_3Y_3, and MX_4Y_2 complexes have two geometric isomers, however, the total number of different isomers possible is 10. The pairwise additivity parameters which must be evaluated for this system are η_{X-X}, η_{X-Y}, and η_{Y-Y}, and once these are known, the chemical shift of M can be calculated by summing the appropriate combination of twelve interaction parameters corresponding to the twelve edges of the octahedral molecule in question. The manner in which this is done is illustrated in Table I for the specific case where X = Cl, Y = Br. The values for η_{X-X} and η_{Y-Y} are obtained by taking one-twelfth of the chemical shift values for MX_6 and MY_6, respectively. The η_{X-Y} value is then obtained by difference from the observed value for either MX_5Y or MXY_5. Where one can observe more than the minimum number of resonance lines necessary to evaluate all the interaction parameters, the best η values are obtained by performing a multiple linear regression analysis with the three η parameters as independent variables.

The application of the pairwise additivity model to a six-coordinate system involving three different ligands, as described in the following section, elicits another significant feature of the model. The η_{i-j} values which are common to both the anion system and the neutral molecular adduct system involving three different ligands have been calculated independently in the two systems and are found to give the same parameter value in both systems. In using the pairwise additivity model to assign spectral lines, it is important to know that the η_{i-j} parameter values can be transferred without variation from one system to another independent of charge type.

It can be seen from Table I that cis and trans isomers of the same "molecule" give different combinations of the interaction parameters and hence are expected to give different chemical shifts for M. This phenomenon of isomer difference has already been observed in the ^{59}Co spectra for $[Co(NH_3)_4(N_3)_2]N_3$ where the cis isomer is shifted 230 ppm downfield from the trans isomer.[14] In the present study, the isomer difference phenomenon, used in conjunction with the pairwise additivity model which predicts the chemical shifts for all isomers whether observed or not, enables the identification of specific isomers where some are present and some are absent.

The $[NbCl_nBr_{6-n}]^-$ System

The ^{93}Nb spectrum of an equimolar mixture of $Et_4N[NbCl_6]$ and $Et_4N[NbBr_6]$ allowed to equilibrate in acetonitrile solution for 1 hr consists of seven lines as shown in the top spectrum of Figure 1. Each line has been assigned to one of the seven possible stoichiometric molecules $[NbCl_nBr_{6-n}]^-$ where $0 \leqslant n \leqslant 6$. The specific assignments given in Table I have been made by interpolating in a sequential manner the lines for the mixed hexahalides between the observed values for the single-line spectra obtained from $[NbCl_6]^-$-MeCN and $[NbBr_6]^-$-MeCN solutions. The variation of signal intensities with systematic variation of the Cl:Br ratio in the solution is consistent with these assignments. These assignments are also consistent with those given recently by Buslaev, *et al.*,[15] and our chemical shift values obtained at 14.67 MHz agree with those obtained earlier at 6 MHz within experimental uncertainty.[16]

Because there are two geometric isomers for each of $[NbCl_2Br_4]^-$, $[NbCl_3Br_3]^-$, and $[NbCl_4Br_2]^-$, a total of ten lines in the nmr spectrum might be anticipated corresponding to the ten different molecules which can in principle be accommodated within the seven possible $[NbCl_nBr_{6-n}]^-$ stoichiometric species. The fact that only seven ^{93}Nb resonances are observed could be due to one or more of the following factors: (i) accidental degeneracy results in two different isomers having the same chemical shift, (ii) a kinetic isomerization process occurring rapidly on the nmr time scale giving rise to a single averaged signal for both cis and trans isomers, and (iii) certain isomers being thermodynamically more stable than others such that not all six isomers from the three geometric pairs exist in detectable concentrations in solution (*i.e.*, <0.05 *M*). The following discussion shows that (iii) is the operative factor in the present case.

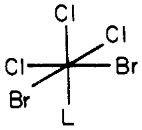
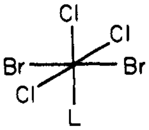
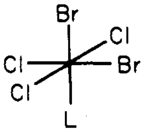
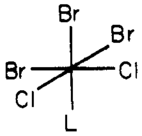
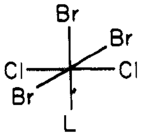
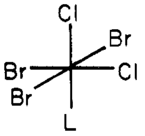
Factor (i) can be ruled out from our knowledge of the dependence of ^{93}Nb shift on its coordinative environment. That the ^{93}Nb shift is *not* a linear function of the coordination composition can be seen from Table I, where the agreement between observed shifts and those calculated using a first-order model is seen to be poor. The agreement between observed and calculated values using the pairwise additivity model indicates the ^{93}Nb shift depends not only upon coordination composition but also upon co-

(14) A. Yamasaki, F. Yajima, and S. Fujiwara, *Inorg. Chim. Acta*, 2, 39 (1968).

(15) Yu. A. Buslaev, V. D. Kopanev, and V. P. Tarasov, *Chem. Commun.*, 1175 (1971).

(16) Buslaev, *et al.*,[15] obtained their $[NbCl_nBr_{6-n}]^-$ data from a solution prepared by dissolving $NbCl_5$ and $NbBr_5$ in acetonitrile. In the absence of added halide ion, this solution could only have yielded hexahaloniobate(V) ions through adventitious hydrolysis since the disproportionation reaction $2MX_5 \cdot MeCN \rightarrow MX_4 \cdot 2MeCN^+ + MX_6^-$ does not occur.[5] On the other hand, if acetonitrile (1 mol of MeCN/mol of Nb) is added to a suspension of Nb_2Cl_{10} in CH_2Cl_2 a clear yellow solution develops immediately from the two-phase mixture. ^{93}Nb nmr indicates the only Nb species present to be $NbCl_5 \cdot MeCN$.

Table II. ^{93}Nb Shifts for the $NbCl_nBr_{5-n}\cdot MeCN$ System in MeCN

	Additivity coeff							
Species	Cl-Cl	Cl-Br	Br-Br	Cl-MeCN	Br-MeCN	δ_{calcd} $\Sigma c_{i-j}\eta_{i-j}$ [a]	δ_{obsd} [b]	δ_{calcd} first order
$NbCl_5\cdot MeCN$	8	0	0	4	0	+48	+49	+49
$NbCl_4Br\cdot MeCN$								
Cis	5	3	0	3	1	−100		−89
Trans	4	4	0	4	0	−84	−90	
$NbCl_3Br_2\cdot MeCN$								
	3	4	1	2	2	−243		
	2	6	0	2	2	−248		−227
	2	5	1	3	1	−225	−229	
$NbCl_2Br_3\cdot MeCN$								
	1	4	3	2	2	−364	−354	
	0	6	2	2	2	−369		−364
	1	5	2	1	3	−386		
$NbClBr_4\cdot MeCN$								
Cis	0	3	5	1	3	−503	−496	−502
Trans	0	4	4	0	4	−524	−529	
$NbBr_5\cdot MeCN$	0	0	8	0	4	−636	−640	−640
$NbCl_6^-$	12	0	0	0	0	−0.7	0	
$NbBr_6^-$	0	0	12	0	0	−730	−731	

[a] Additivity parameter values (ppm): $\eta_{Cl-Cl} = 0$; $\eta_{Cl-Br} = -32.8$; $\eta_{Br-Br} = -60.8$; $\eta_{Cl-MeCN} = +12.0$; $\eta_{Br-MeCN} = -37.3$. [b] Error limits on observed shifts are ±5 ppm.

ordination geometry. Data in Table I indicate a minimum difference of 5 ppm between cis and trans isomers of the same coordination composition, which difference is capable of resolution with the present instrumentation. Factor (ii) can be ruled out by observing the growth of the ^{93}Nb lines in the spectrometer as the redistribution reaction proceeds. The fact that this growth can be observed indicates that the rate of *intermolecular* halogen exchange is slow on the nmr time scale. This does not, however, rule out the possibility of an *intramolecular* rearrangement leading to isomerization which might be more rapid. To rule out this possibility, the line shapes observed for the $n = 2$-4 cases show no evidence of distortion which could be attributed to exchange broadening. Thus if isomerization is occurring, it is doing so at a rate sufficiently rapid to give "sharp" lines whose positions are definitive. The comparison in Table I of the calculated line positions with the observed positions based on the assumed presence of only one geometric isomer shows agreement within 1 ppm. If a rapid isomerization process were occurring, the observed line position would represent the weighted average for the static isomers, whose two line positions would be in poor agreement with the

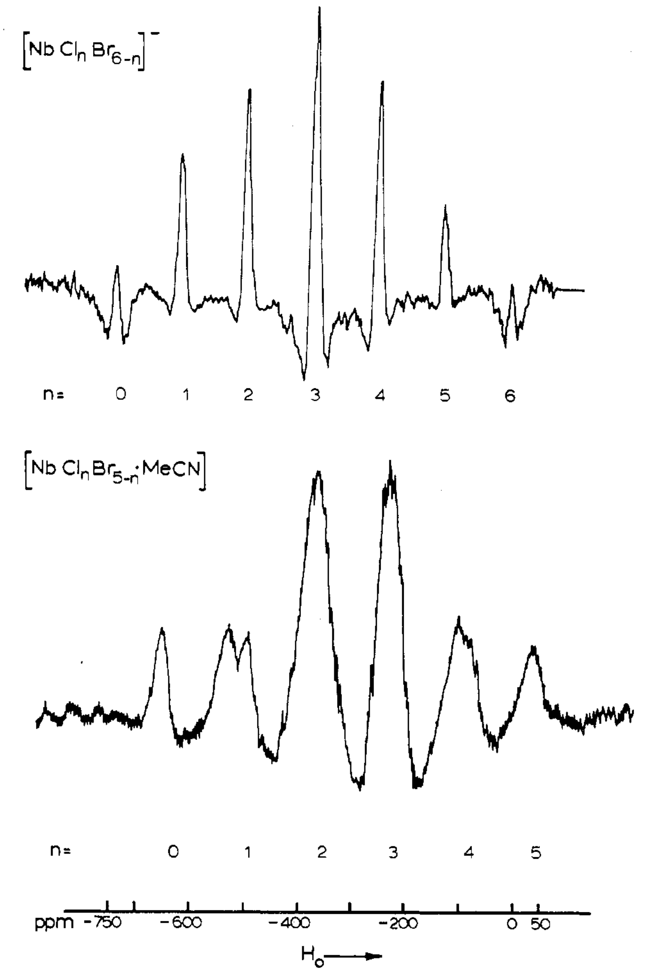


Figure 1. Niobium-93 nmr spectra of $[NbCl_nBr_{6-n}]^-$ and $NbCl_nBr_{5-n}\cdot MeCN$ systems in acetonitrile solution. Relative line intensities have been instrumentally adjusted to provide an effective comparison of line positions and do not, therefore, provide a measure of the relative concentrations of the different species in solution.

calculated values. The weight of evidence therefore indicates that factor (ii) is not operating.

Having accepted the fact that for each of $[NbCl_2Br_4]^-$, $[NbCl_3Br_3]^-$, and $[NbCl_4Br_2]^-$, one geometric isomer predominates to the virtual exclusion of the other, we are then faced with the problem of identifying, in each case, which isomer this is. To accomplish this we require a theoretical model capable of reflecting the geometry dependence of the metal atom chemical shift in a six-coordinate complex. The pairwise additivity model which has been successfully applied to metal atom shifts in four-coordinate complexes possesses this added capability when extended to the six-coordinate case. Theoretical chemical shift values calculated as shown in Table I for the six isomers from the three cis-trans pairs indicate that in every case only the cis isomer is present in solution.

The $NbCl_nBr_{5-n}\cdot MeCN$ System

By dissolving either Nb_2Cl_{10} or Nb_2Br_{10} in acetonitrile solution under anhydrous conditions, a solution results which gives rise to a single broad ^{93}Nb resonance line which can only be assigned to the solvent adduct $NbX_5\cdot MeCN$, as shown below.

Adduct	^{93}Nb shift, ppm	Line width, Hz
$NbCl_5\cdot MeCN$	+49	*Ca.* 500
$NbBr_5\cdot MeCN$	−640	*Ca.* 500

By mixing equivalent amounts of the anhydrous $NbCl_5\cdot MeCN$ and $NbBr_5\cdot MeCN$ solutions, a new solution giving a seven-line ^{93}Nb spectrum results, as shown at the bottom of Figure 1. The assignments of these spectral lines to the six possible stoichiometries in the system $NbCl_nBr_{5-n}\cdot MeCN$ ($0 \leqslant n \leqslant 5$) are given in Table II. An identical spectrum was observed for a 1:1:4 solution of Nb_2Cl_{10}-Nb_2Br_{10}-MeCN in CH_2Cl_2, the only difference being that all resonances were shifted downfield by 27 ± 3 ppm. Such solvent shifts are not unusual and generally signify greater stabilization of either the ground or excited electronic states of a species in one solvent relative to the other. The intensities of all observed lines are approximately those anticipated for the 1:5:10:10:5:1 random distribution of two ligands among five coordination positions.

All of these solutions produced identical spectra after standing for 2 weeks. This indicates the absence of hydrolysis or any autoionization process capable of producing $[NbX_nY_{6-n}]^-$ species in sufficient concentration to be detected.

Addition of small amounts of "wet" acetonitrile or free halide ion to the $NbCl_nBr_{5-n}\cdot MeCN$ solution in acetonitrile results in the appearance of another series of sharper resonance lines ($\nu_{1/2} \leqslant 100$ Hz) characteristic of the $[NbCl_nBr_{6-n}]^-$ system coexisting with the relatively broad resonances ($\nu_{1/2} \approx 500$ Hz) due to the MeCN adduct species. If sufficient halide ion or "wet" acetonitrile is added, only the seven-line $[NbCl_nBr_{6-n}]^-$ spectrum is observed. Similar treatment of the $NbCl_nBr_{5-n}\cdot MeCN$ system in dichloromethane solution with "wet" dichloromethane results in a gradual collapse of the ^{93}Nb spectrum and simultaneous formation of a precipitate in the sample tube.

It is evident that the agreement between the observed shift values and those calculated using the pairwise additivity model is not as good as in the previous system where there are only two different types of substituent on the niobium atom. The increased error limits on the latter set of data result in large part from the broader resonance lines[17] observed for the $NbX_nY_{5-n}\cdot MeCN$ system (*ca.* 500 Hz *vs.* *ca.* 100 Hz for the $[NbX_nY_{6-n}]^-$ anions) making the determination of line position less precise. Even with the increased error limits, however, it is still possible to assign the signals for cis and trans isomers of $NbClBr_4\cdot MeCN$.

By using the pairwise additivity model, structural information about the MeCN adducts in acetonitrile solution is readily extracted. A transfer of the η_{i-j} parameter values from the $[NbCl_nBr_{6-n}]^-$ system permits a calculation of $\eta_{Cl-MeCN}$ and $\eta_{Br-MeCN}$ values from the observed shifts of the pentachloride and pentabromide adducts, respectively. Using these parameter values, a preliminary set of chemical shifts for the twelve possible structures of the six stoichiometries were calculated. A basis matrix containing the structure coefficients and the observed chemical shifts was then subjected to a multiple linear regression analysis to obtain the best values for the η_{i-j} parameters. The results are presented in Table II. These show that in the case of $NbClBr_4\cdot MeCN$, both the cis and trans isomers are present. In the other cases where more than one geometric isomer is possible, only one isomer is observed.

Geometric Preferences

The $[NbCl_nBr_{6-n}]^-$ System. If viewed on a purely steric

---

[17] Because of its large electric quadrupole moment, the niobium nucleus experiences increased quadrupolar relaxation and hence increased line width in the presence of an increased electric field gradient. The substitution of an MeCN molecule for a halogen in a hexahaloniobate ion will provide this electrical asymmetry.

basis, the preference for cis configurations displayed by this system might appear surprising. The results are, however, consistent with a pattern already established for six-coordinate tin halides $[SnX_nY_{6-n}]^{2-}$ and titanium halides $[TiX_nY_{6-n}]^{2-}$. Infrared and Raman studies indicate the adoption of cis configurations by $[SnCl_4Br_2]^{2-}$, $[SnCl_4I_2]^{2-}$, $[SnCl_2Br_4]^{2-}$, and $[SnCl_2I_4]^{2-}$ in the solid state.[18]

Similar evidence has been adduced to indicate cis configurations for $[TiCl_2Br_4]^{2-}$ and $[TiCl_4Br_2]^{2-}$.[18] Studies by ^{19}F nmr show that $[SnF_4X_2]^{2-}$ species (X = Cl, Br, I) favor the cis over the trans configuration, the preference increasing from Cl to Br to I.[19]

Zahrobsky[20] has recently introduced a model based upon steric interaction which predicts that in MA_4B_2 complexes, the cis isomer will always be favored over the trans isomer irrespective of the relative sizes of A and B. The preference for cis configurations has also been rationalized in terms of the enhanced π bonding which can occur relative to that which might be possible in a trans isomer.[18]

The $NbCl_nBr_{6-n}$·MeCN System. In the $[NbCl_nBr_{6-n}]^-$ system, it was noted that cis geometries are preferred to trans. Alternatively, one can say that Br prefers to be trans to Cl rather than to Br. The order of stability is then (Br trans to Cl) > (Br trans to Br). A similar analysis of the observed isomeric preferences in the MeCN adduct system indicates the following order of stability:[21] (Br trans to MeCN) > (Br trans to Cl) > (Cl trans to MeCN) ≈ (Br trans to Br).

Experimental Section

Instrumentation. Niobium-93 nmr spectra were obtained at 14.67 MHz using a Varian 4200 B wide-line spectrometer with a V-4210A variable-frequency oscillator and a V-3400 9-in. magnet with Fieldial stabilization and sweep capability. Resonance lines were recorded as derivatives of dispersion signals and calibration was effected by the generation of audiofrequency side bands. Minimum detection sensitivity for niobium species under these conditions is about 0.05 *M*. Chemical shift values, designated by δ, are quoted in parts per million (ppm) relative to the $NbCl_6^-$ signal, with positive shifts denoting increased shielding. All spectra were measured at room temperature. Quoted errors in δ values are standard deviations and result from calibration uncertainty.

Materials. Solvents (acetonitrile and methylene chloride) were rigorously dried by prolonged reflux over, and fractional distillation from, calcium hydride while under a dry nitrogen atmosphere. High-purity niobium pentachloride and pentabromide were used as received from Alfa Inorganics. Tetraethylammonium and potassium chlorides and bromides were dried by standard techniques. Tetraethylammonium hexachloroniobate(V) and hexabromoniobate(V) were prepared as described previously[4,6,8] in the appropriate redistilled thionyl halide. Niobium oxide trichloride was prepared as described in the literature.[8] All sample preparations and manipulations were performed under dry nitrogen.

$[NbCl_nBr_{6-n}]^-$ Solutions. The following solutions were prepared in dry acetonitrile: $Et_4N[NbCl_6] + Et_4N[NbBr_6]$, $Et_4N[NbCl_6] + NbBr_5 + KBr$, $Et_4N[NbCl_6]$ + excess KBr, $NbCl_5$ + excess KBr, $NbBr_5$ + excess KCl, $NbCl_5$ + excess Et_4NBr, and $NbCl_5 + KCl + NbBr_5 + KBr$. All of these solutions gave rise to similar seven-line ^{93}Nb spectra. The resonance positions and line shapes were found to be independent of the cation present and of the Cl:Br:Nb ratio. The intensities of the observed lines within a particular spectrum varied with the Cl:Br:Nb ratio as expected for a random redistribution of halogens among $[NbCl_nBr_{6-n}]^-$ species. Total niobium concentration was generally in the range of 0.5–1 *M*.

$NbCl_nBr_{5-n}$·MeCN Solutions. The following solutions were prepared in dry acetonitrile or dichloromethane or in a 50 mol % mixture of the two solvents.

Solute (X = Cl, Br)	Solvents
$NbX_5\cdot MeCN$	MeCN; CH_2Cl_2
Nb_2X_{10}	MeCN; 50 mol % MeCN–CH_2Cl_2
Nb_2X_{10} + 2MeCN	CH_2Cl_2
$Nb_2Cl_{10} + Nb_2Br_{10}$	MeCN; 50 mol % MeCN–CH_2Cl_2
$Nb_2Cl_{10} + Nb_2Br_{10}$ + 4MeCN	CH_2Cl_2

Identical resonance shapes and positions were observed for each assigned species within the same solvents. A systematic solvent dependence of the chemical shift, forcing to lower field, was observed upon changing from pure MeCN to 50 mol % MeCN–CH_2Cl_2 to pure CH_2Cl_2. Total niobium concentration was generally in the vicinity of 1.5 *M*.

Potential Impurities. Because of the high affinity of niobium for oxygen, it is possible that oxyhaloniobates could arise as impurities in the solutions under study. The ^{93}Nb spectra for these potential impurities in acetonitrile solution were obtained by preparing niobium oxide trichloride according to the published procedure[22] and then adding excess chloride ion to this solution to obtain the higher chlorides. A similar procedure was used for the oxybromoniobates, except in this case the pure niobium oxide tribromide was not isolated. The ^{93}Nb spectra observed for these species were as follows.

Solute in MeCN	^{93}Nb shift, ppm	Line width, Hz
$NbOCl_3$	503	700
$[NbOCl_{3+n}]^{n-}$ ($n \simeq 2$)	482	200
$[NbOBr_{3+n}]^{n-}$ ($n \simeq 2$)	200	200

No resonance lines having these characteristics were observed in any of the other systems studied.

Registry No. $NbCl_6^-$, 21640-06-2; $NbCl_5Br^-$, 34373-30-3; *cis*-$NbCl_4Br_2^-$, 40354-71-0; *cis*-$NbCl_3Br_3^-$, 40354-72-1; *cis*-$NbCl_2Br_4^-$, 40354-73-2; $NbClBr_5^-$, 34371-96-5; $NbBr_6^-$, 32965-80-3; $NbCl_5\cdot MeCN$, 21126-02-3; *trans*-$NbCl_4Br\cdot MeCN$, 40354-76-5; $NbCl_3Br_2\cdot MeCN$, 40354-77-6; $NbCl_2Br_3\cdot MeCN$, 40354-78-7; *cis*-$NbClBr_4\cdot MeCN$, 40354-79-8; *trans*-$NbClBr_4\cdot MeCN$, 40354-80-1; $NbBr_5\cdot MeCN$, 21126-01-2; niobium-93, 7440-03-1.

Acknowledgments. This work was supported by the National Research Council of Canada through Operating Grant No. A-1906 to R. G. K. and through an NRC scholarship to H. G. S.

---

(18) R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, 7, 1603 (1968).

(19) P. A. W. Dean and D. F. Evans, *J. Chem. Soc. A*, 1154 (1968).

(20) R. F. Zahrobsky, *J. Amer. Chem. Soc.*, 93, 3313 (1971). We are grateful to a referee for drawing this model to our attention.

(21) There is one outstanding exception to this trend; that is the resonance at −529 ppm which is assigned to *trans*-$[NbClBr_4\cdot MeCN]$.

(22) F. Fairbrother, A. H. Cowley, and N. Scott, *J. Less-Common Metals*, 1, 206 (1959).