Niobium-93 Nuclear Quadrupole Resonance Studies of Niobium Pentafluoride and its Complexes with Xenon Difluoride and some Organic Bases ‡

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^{93}Nb N.q.r. spectra of NbF_5, XeF_2,NbF_5, $XeF_2,2NbF_5$, NbF_5,L ($L = Me_2O$ or CH_2ClCN), and $NbF_5,2py$ have been obtained. The results are consistent with low values of the asymmetry parameter (η) for the electric field gradient tensor at the ^{93}Nb nuclei in all compounds investigated. A simple point-charge model is used to derive a semi-quantitative measure of the interaction between XeF^+ and NbF_6^- or $Nb_2F_{11}^-$ ions in xenon difluoride–niobium pentafluoride complexes.

THEORETICAL and experimental studies of nuclear quadrupole resonance have shown that nuclear quadrupole coupling parameters in solid molecular compounds are normally not very different from those found for isolated molecules in the gas phase. Resonance frequencies of solids can give information about the chemical bonds in the samples as well as information relating to the structure of the lattices.[1,2] Few studies[3] of ^{93}Nb n.q.r. frequencies have been reported, but the ^{93}Nb nucleus is interesting because its high nuclear spin (9/2) simplifies determination of the asymmetry parameter (η) of the electric field gradient tensor at the nucleus.

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‡ No reprints available.

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1 : 1 and 1 : 2 Complexes of XeF_2 with many pentafluorides are known (*e.g.* see refs. 4—6) and there has been some discussion over their formulation. Raman spectra of some complexes have been interpreted in terms of the ionic species XeF^+, MF_6^-, or XeF^+, $M_2F_{11}^-$ (M = As, Ru, Pt, Ir, Os, or Sb).[4] However, an *X*-ray crystallographic study of $XeF_2,2SbF_5$ has been interpreted to mean that, if the compound is considered in terms of the ions $XeF^+ + Sb_2F_{11}^-$, there is considerable interaction between the ions (see Figure 1).

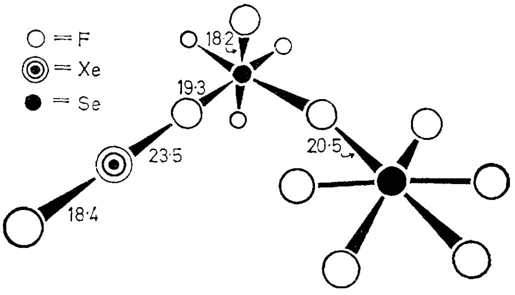

FIGURE 1 Structure of XeF_2—$2SbF_5$ with relevant bond lengths shown in nanometers

The n.q.r. method differs from standard conductivity methods of investigating this problem in that it provides information about the electronic distribution within the solid complexes themselves rather than about the free energy of dissociation of the units, in the melt, into ionic species.

TABLE 1

^{93}Nb N.q.r. parameters of NbF_5

Temp. *T*/K Group	Transition	*E*/MHz	Intensity	Frequency ratio	η	$\lvert e^2qQ\rvert$/MHz
77 Group one	9/2–7/2	19·478 *	s	1·3396	0·20 ± 0·03	117·3 ± 0·2
	7/2–5/2	14·54	s			
	5/2–3/2	n.o.				
77 Group two	9/2–7/2	19·057 *	s	1·3411	0·23 ± 0·04	114·7 ± 0·3
	7/2–5/2	14·21	s			
	5/2–3/2	n.o.				
273 Group one	9/2–7/2	19·270 *	vs	1·3355	0·13 ± 0·02	115·80 ± 0·03
	7/2–5/2	14·429	s	1·526	0·13 ± 0·01 *	
	5/2–3/2	9·458	mw	1·659	0·14 ± 0·02	
	3/2–1/2	5·70	vw			
273 Group two	9/2–7/2	19·002 *		1·334	0·17 ± 0·02	114·29 ± 0·05
	7/2–5/2	14·208		1·540	0·17 ± 0·01 *	
	5/2–3/2	9·227	mw	1·66	0·16 ± 0·02	
	3/2–1/2	5·70	vw			

* Most reliable values, used for calculation of e^2qQ.

N.q.r. studies of some NbF_5 organic base complexes were undertaken to investigate the feasibility of use of the n.q.r. method to study interactions between the bases and the central metal atom.

Measured N.Q.R. Frequencies and Calculation of η *and* e^2qQ.—The secular equation for a system with $J = 9/2$ has been solved for many values of η.[7,8] In this work values of η were found by comparing the ratios of experimentally observed resonance frequencies with graphs, of the theoretical ratios (calculated from the data of Reddoch[7]) plotted against η. In samples where three or more transitions were observed, for a given environment of the nucleus, unambiguous assignment of the resonances was possible by comparison of theoretical and experimenta ratios for two, or more, pairs of resonances. In some samples only two transitions were observed and in these cases it has been assumed that the resonances observed correspond to the 9/2–7/2 and 7/2–5/2 transitions which are the highest energy transitions for the 9/2 spin system when $\eta < 0{\cdot}6$. It is extremely unlikely that η exceeds 0·6 in the compounds investigated here.

The observed n.q.r. data and values of e^2qQ and η found from this data are listed in Tables 1—3. The resonance lines were generally quite broad (20—100 kHz) and varied widely in intensity and shape. For compounds where two resonances were observed for each nuclear quadrupole transition, because of physically different environments of the ^{93}Nb nucleus, the resonance frequencies are listed in groups in which the ratios of the frequencies satisfy the predicted relationships[7,8] for transitions of a 9/2 spin system. Resonance frequencies, and ratios of resonance frequencies considered most reliable for calculation of e^2qQ and η are marked with an asterisk. Where it has been possible to calculate η from more than one ratio of resonance frequencies this has been done to show that values agree within the limits of experimental error. Tolerances given for η and e^2qQ take into account possible errors in measurement of resonance frequencies and in graphical determination of η. Tolerances in values of η are quite large because at small values of η the energy levels of the 9/2 spin system are not very dependent on the value of η.

DISCUSSION

Point change approximations have been successfully used for correlating nuclear quadrupole coupling con-

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TABLE 2

^{93}N.q.r. parameters of complexes of NbF_5,XeF_2 and $(NbF_5)_2XeF_2$

Atom	Temp. T/K Group Nb_2F_{10},XeF_2	Transition	E/MHz	Intensity	Frequency ratio	η	$\lvert e^2qQ\rvert$/MHz
Nb [1]	77	9/2–7/2	18·621 *	s	1·3357	0·11 ± 0·05 *	111·85 ± 0·10
	Group one	7/2–5/2	13·940	s	1·498	0·0 ± 0·07	
		5/2–3/2	9·30 †	m			
		3/2–1/2	n.o.				
Nb [1]	77	9/2–7/2	18·208 *	s	1·3354	0·12 ± 0·03 *	109·38 ± 0·11
	Group two	7/2–5/2	13·635	s	1·498	0·0 ± 0·13	
		5/2–3/2	9·10 †	m			
Nb [2]	77	9/2–7/2	12·665 *	m	1·336	0·14 ± 0·07	76·1 ± 0·2
	Group one	7/2–5/2	9·48 †	m			
		5/2–3/2	n.o.				
Nb [2]	77	9/2–7/2	12·17 *	m	1·337	0·17 ± 0·13	73·2 ± 0·5
	Group two	7/2–5/2	9·10 †	m			
		5/2–3/2	n.o.				
Nb [1]	290	9/2–7/2	18·20 *	ms	1·333	0·0 ± 0·1 *	109·2 ± 0·3
		7/2–5/2	13·65	ms	1·50	0·0 ± 0·2	
		5/2–3/2	9·1 †	m			
Nb [2]	290	9/2–7/2	12·185 *	m	2·017	0·08 ± 0·03	73·15 ± 0·11
		7/2–5/2	9·1 †	m			
		5/2–3/2	6·06	w			
NbF_5,XeF_2	77	9/2–7/2	5·70 *	s	1·36	0·4 ± 0·4	34·6 ± 0·8
		7/2–5/2	4·2	w			
	273	9/2–7/2	5·65 *	s	1·35	0·3 ± 0·3	34·2
		7/2–5/2	4·2	w			

* Most reliable values, used for calculation of e^2qQ. † These levels overlap with each other.

TABLE 3

^{93}Nb N.q.r. parameters of complexes of NbF_5 with organic bases

Temp. T/K Group	Transition	E/MHz	Intensity	Frequency ratio	η	$\lvert e^2qQ\rvert$/MHz
NbF_5Me_2O						
77	9/2–7/2	14·212 *	s	1·331	0·0 ± 0·06	86·19 ± 0·08
Group one	7/2–5/2	10·603 *	s	1·5028	0·02 ± 0·03 *	
	5/2–3/2	7·047	ms			
77	9/2–7/2	14·138 *	s	1·340	0·2 ± 0·2	84·86 ± 0·05
Group two	7/2–5/2	10·603	s	1·5046	0·04 ± 0·05 *	
	5/2–3/2	7·047	ms			
273	9/2–7/2	14·359 *	s	1·331	0·0 ± 0·06	86·19 ± 0·08
	7/2–5/2	10·768	s	1·5028	0·02 ± 0·03 *	
	5/2–3/2	7·165	ms			
NbF_5,CH_2ClCN						
77	9/2–7/2	16·63 *	m	1·33	0·0 ± 0·1 *	99·8 ± 0·20
	7/2–5/2	12·551	m	1·51	0·06 ± 0·1	
	5/2–3/2	8·31	vw			
273	9/2–7/2	16·814 *	m	1·333	0·00 ± 0·04	100·92 ± 0·07
	7/2–5/2	12·618	m	1·507	0·04 ± 0·04 *	
	5/2–3/2	8·375	m			
(Despite careful searching the chlorine n.q.r. could not be detected)						
$NbF_5,2py$						
77	9/2–7/2	16·02 *	m	1·33	0·0 ± 0·2	96·1 ± 0·5
	7/2–5/2	12·02	m			
	5/2–3/2	n.o.				
273	9/2–7/2	16·695 *	ms	1·3341	0·05 ± 0·06	100·33 ± 0·04
	7/2–5/2	12·514	ms	1·5161	0·10 ± 0·01 *	
	5/2–3/2	8·254	m			

* Most reliable values used for calculation of e^2qQ.

stant data with known geometric features of the chemical environment of nuclei with quadrupole moments (*e.g.* see refs. 9—12).

In the point change model, as we will use it here, a number of electrons, n_i, in an orbital directed at angle θ to a principal axis, j, of the electric field gradient tensor is considered to give the contribution (1) to the gradient

$$V_{jj(i)} = K'n_i \frac{3\cos^2\theta - 1}{\langle r^3\rangle_{Av}} \qquad (1)$$

of electrostatic potential along the j axis. In expression

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[11] B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *J. Chem. Soc.* (*A*), 1969, 143.

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(1), r is the distance between the electrons and the nucleus and K' is a constant. We also make the approximation that electrons on other atoms and filled shells on the niobium atom give negligible contributions to the field gradient at the niobium nucleus. In the niobium compounds considered here it may be assumed that, in the region of the ^{93}Nb nucleus, the nature of the niobium valence orbitals is independent of the atom towards which the orbitals are directed.

Thus $\langle r_i^3\rangle_{Av}$ can be included in a new constant K which is approximately the same in all cases and may be left out of further discussion. Values of e^2qQ, and η for four octahedral, and pseudo-octahedral environments, calculated by this method, are given in Table 4.

TABLE 4

Nuclear quadrupole coupling constants and asymmetry parameters for nuclei in pseudo-octahedral environments

Structure	e^2Qq	η
Symmetrical octahedron	0	0
C_{4v} Monosubstituted octahedron	$K2(n_F - n_X)$	0
cis-Symmetrically disubstituted octahedron	$-K2(n_F - n_X)$	0
trans-Symmetrically disubstituted octahedron	$K4(n_F - n_X)$	0

The constant K also includes the factors relating the coupling constant expressed in MHz to the z component of the electric field gradient tensor.

Niobium Pentafluoride.—The observed n.q.r. spectrum of NbF_5 at 273 and 77 K (Table 1) indicates that niobium atoms with two physically different environments are present. A possible very weak peak *ca.* 5·7 MHz in the n.q.r. spectrum of NbF_5 is tentatively attributed to the 1/2—3/2 transition. It is not essential to the arguments which follow.

NbF_5 Crystallises in the $C_{2/m}$ space group (No. 12) with two tetrameric units in the crystallographic unit cell [13] (*i.e.* one per primitive, or Bravais unit cell [14]). In each tetramer there are two niobium atoms with site symmetry C_2 (g sites) and two with site symmetry C_s (i sites). No significant differences in chemical environment are detectable by X-ray single-crystal techniques.[13] The differences found in e^2qQ for the two environments (*ca.* 3% at 77 K) are compatible with either intermolecular fields or slight distortions of bond lengths and angles due to packing strains in the crystals.

The deviation of η from the value of zero to be expected for a regular, *cis*-disubstituted, octahedron is attributed to the observed distortion of the bond angles from 90°.[13] $NbCl_5$ Crystallises in dimeric units with the ^{93}Nb nuclei at the centres of distorted octahedra of chlorine atoms in which two chlorine atoms (*cis* to each other) are shared with adjacent niobium atoms.[15] In this environment $e^2qQ \simeq 78$ MHz and $\eta \simeq 0{\cdot}32$.[3] The smaller values of η in Nb_4F_{20} tetramers are consistent with the fact that the observed deviations from 90° bond angles are smaller for NbF_5 tetramers than for $NbCl_5$ dimers.[13,15]

XeF_2,NbF_5 *and* $XeF_2,2NbF_5$.—The observed quadrupole coupling constant for ^{93}Nb in XeF_2,NbF_5 (34·6 MHz at 77 K) is much greater than would be expected from a structure involving NbF_6 ions. In the latter case only a very small field gradient is expected since it could arise only from the lattice or through deviations from regular octahedral symmetry. It is concluded therefore that one of the niobium–fluorine bonds is altered through participation in a fluorine bridge.

The structure of $XeF_2,2NbF_5$ has not been determined but it may be assumed, by analogy with $XeF_2,2SbF_5$,[6] that a unit approximating to $Nb_2F_{11}^-$ is present. In $XeF_2,2SbF_5$ the XeF–Sb bridge is *cis* to the Sb–F–Sb bridge (see Figure 1). Our results show that a similar geometry is present in $XeF_2,2NbF_5$. The argument is given below.

The n.q.r. data for NbF_5 and NbF_5,XeF_2 is first used to obtain values for $K(n_F - n_X)$ using the appropriate expressions in Table 4. These values are then used in the corresponding expressions for both the *cis* and *trans* structures for $XeF_2,2NbF_5$ to predict e^2qQ for both niobium nuclei. In Table 5 n_{F_b} and b_{F_b}, are orbital occupation factors for niobium orbitals directed towards bridging fluorine atoms in the Nb–F–Nb and NbF–Xe bridge respectively. Superscripts 1, 2 refer to the metal atoms as labelled in Figures 2(a) and (b). Where crystal splittings were observed average values of e^2qQ are used.

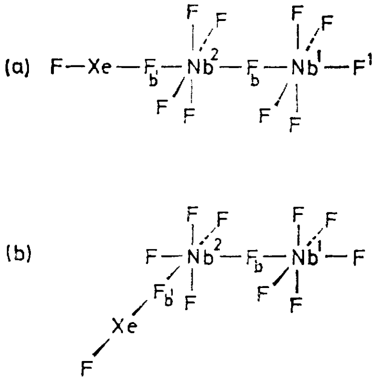

FIGURE 2 Possible structures of $XeF_2,2NbF_5$: (a) *trans*; (b) *cis*

The agreement between the observed and predicted coupling constants for the *cis* structure is excellent and strongly suggests that the structure of $XeF_2,2NbF_5$ approximates to that shown in Figure 2(b). This structure will be assumed in further discussion. Either of the structures 2(a) or (b) are expected to have a small asymmetry parameter. The latter, however, is much more affected by deviation of the bond angles from 90° than is the coupling constant, and the small values found for η in $XeF_2,2NbF_5$ are quite consistent with the postulated structures.

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[13] A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.

[14] P. J. Hendra and T. R. Gilson, ' Laser Raman Spectroscopy,' Wiley, 1970.

[15] A. Zalkin and D. E. Sands, *Acta Cryst.*, 1958, **11**, 615.

It also follows from the predictions of Table 4 and the experimental results that

$$\frac{n_{\mathrm{F}} - n_{\mathrm{F}_{b'}} \text{ (in XeF}_2\text{,NbF}_5)}{n_{\mathrm{F}} - n_{\mathrm{F}_b} \text{ (for Nb}^1 \text{ in XeF}_2\text{,2NbF}_5)} = \frac{34{\cdot}6}{110{\cdot}6} \simeq 0{\cdot}31$$

and

$$\frac{n_{\mathrm{F}} - n_{\mathrm{F}_{b'}} \text{ (for Nb}^1 \text{ in XeF}_2\text{,2NbF}_5)}{n_{\mathrm{F}} - n_{\mathrm{F}_b} \text{ (for Nb}^1 \text{ in XeF}_2\text{,2NbF}_5)} = 2\,\frac{2 \times 74{\cdot}6 - 110{\cdot}6}{110{\cdot}6} \simeq 0{\cdot}35$$

This means that in NbF_6^- the decrease in electron density in the Nb valence orbital directed towards a fluorine atom when that fluorine atom is brought into contact with an XeF^+ species is 31% of that which occurs when the fluorine atom is bridge-bonded to another NbF_5 unit. In $XeF^+Nb_2F_{11}^-$ the corresponding decrease in electron density in the orbital directed towards the fluorine atom forming a bridge to the xenon is 35% of that in the orbital directed towards fluorine bridge-bonded to another niobium atom. If the value of $n_{\mathrm{F}} - n_{\mathrm{F}_b} = 116{\cdot}0$ MHz obtained from NbF_5 at 77 K is used the decreases are 29·7 and 28·6% for $XeF^+NbF_6^-$ and $XeF^+Nb_2F_{11}^-$ respectively.

These results suggest that the Xe–F–Nb bridges in XeF_2,NbF_5 and $XeF_2,2NbF_5$ are very similar. The calculations also yield a semi-quantitative measure of the interaction between the ions which are potentially present in the solid state. The reliability of this treatment is difficult to estimate at present but we suggest that similar studies, of other compounds containing bridging fluorine atoms and nuclei with quadrupole moments (*e.g.* TaF_5, SbF_5, NbF_5,SbF_5, and their complexes with XeF_2, SF_4, SeF_4, BrF_3, *etc.*) may prove both interesting and useful.

Complexes of Niobium Pentafluoride with Organic Bases (Table 3).—The n.q.r. spectrum of NbF_5,Me_2O at 77 K indicates that two physical environments are present for the ^{93}Nb nuclei whilst the spectrum at 273 K indicates the presence of only one environment. It is concluded that there is a phase change between these temperatures. The niobium n.q.r. spectra of NbF_5,Me_2O and NbF_5,CH_2ClCN are consistent with the presence of pseudo-octahedral (C_{4v}) symmetry at the niobium atom.[16] In this environment both distortion of bond angles from the 'ideal' octahedral angles, and asymmetry of the base give contributions to asymmetry in the electric field gradient tensor at the ^{93}Nb nucleus. In both complexes the experimental values of η are small indicating that both effects are slight.

TABLE 5

Predicted and observed n.q.r. parameters for $XeF_2,2NbF_5$

Molecule	Expression for e^2Qq	e^2Qq Observed (MHz at 77 K)	e^2Qq Calculated (MHz)
NbF_5	$K(2n_{\mathrm{F}} - 2n_{\mathrm{F}_b})$	116·0	
$F{-}Xe{-}F{-}NbF_5$	$K(2n_{\mathrm{F}} - 2n_{\mathrm{F}_{b'}})$	34·6	
Structure of Figure 2(a) (*trans*)	Nb¹; $K(2n_{\mathrm{F}} - 2n_{\mathrm{F}_b})$		116
	Nb²; $K(2n_{\mathrm{F}} - 2n_{\mathrm{F}_b}) + K(2n_{\mathrm{F}} - 2n_{\mathrm{F}_{b'}})$		150·6
Structure Figure 2(b) (*cis*)	Nb¹; $K(2n_{\mathrm{F}} - 2n_{\mathrm{F}_b})$		116
	Nb²; $K(n_{\mathrm{F}} - n_{\mathrm{F}_b}) + K(n_{\mathrm{F}} - n_{\mathrm{F}_{b'}})$		75·3
$XeF_2,2NbF_5$	Nb¹	110·6	
	Nb²	74·6	

The n.q.r. spectrum of the 1 : 2 complex $NbF_5,2py$ shows that ^{93}Nb nuclei have been detected in only one physical and chemical environment, and that in this environment $\eta = 0$. ^{19}F N.m.r. spectra of this pyridine complex in solution have been interpreted in terms of an ionic structure[17] ($NbF_6^-,NbF_4,4py^+$) but there is, as yet, no conclusive evidence that this structure is retained in the solid state.[16] The point charge model has been used to predict the value of η and e^2qQ for the ^{93}Nb nucleus in as many as feasible of the seven- and eight-coordinate environments for solid $NbF_5,2py$. However, η is predicted to be zero for several of these environments, and for many others it is not possible to prove that $\eta \neq 0$ so that n.q.r. measurements on their own give no new knowledge of the structure of $NbF_5,2py$.

EXPERIMENTAL

NbF_5 Was prepared by fluorination of 'Specpure' niobium metal at 150 °C with a nitrogen–fluorine mixture. The NbF_5 was further purified before use by sublimation in a carefully degassed, greaseless, glass vacuum line fitted with Teflon taps. Preparation of complexes of NbF_5 with organic bases has been described elsewhere.[16]

The preparations of XeF_2,NbF_5 and $XeF_2,2NbF_5$ were carried out in Pyrex glass vessels fitted with glass-to-metal seals and small brass valves which were attached to a stainless steel and nickel vacuum manifold.[5] The reaction vessels were baked under vacuum and preseasoned, first with ClF_3 and then XeF_2, before use. Known weights of NbF_5 were introduced into the tared reactors in a dry box. After the vessels had been pumped and weighed XeF_2 was condensed into them until the required stoicheiometries were attained. The mixtures were fused and pumped to constant weight as described elsewhere.[17] Final weights indicated the stoicheiometries $XeF_2,1{\cdot}07NbF_5$ (total weight of sample 1·6910 g) and $XeF_2,1{\cdot}95NbF_5$ (total weight of sample 1·7076 g). The compounds were powdered and introduced into Pyrex ampoules.

N.q.r. spectra in the range 4—50 MHz were obtained using both a Decca Radar n.q.r. spectrometer and a locally constructed spectrometer. Both instruments are super-regenerative and have automatic frequency calibration and sideband suppression facilities.[18-20] Overnight sweeps without sideband suppression but with automatic frequency calibration and covering a two to one frequency range were first carried out for each sample until the whole frequency

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range from 4 to 50 MHz had been examined at both 77 and 273 K. Zeeman modulation was used during this search procedure. Detected resonances were then re-examined using expanded sweeps with sideband suppressions and with frequency calibration markers at 10 kHz intervals.

The sample temperature was controlled by immersing the probe assembly in liquid nitrogen or an ice slush, and measured automatically using a copper–Constantan thermocouple in contact with the probe.[21] Intermediate temperatures were achieved by allowing the probe, precooled in liquid nitrogen, to warm slowly in a Dewar vessel. The thermal capacity of the probe was made high enough to give a suitably low rate of temperature rise.

Despite the use of Zeeman modulation some trouble was initially experienced from spurious signals in the region below 10 MHz. Improvement was obtained by orienting the r.f. chokes in the oscillator unit orthogonally to the Zeeman coil (a single short solenoid coaxial with the r.f. coil and wound around the outside of a 5-in Dewar vessel) and by using a magnetic shield immediately beneath the r.f. unit. In this frequency range and with weak resonances duplicate runs were carried out both with and without the sample present.

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