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The Exchange of Water and Chloride Ion with Nickel(II)–Chloride Complexes by Nuclear Magnetic Resonance in Concentrated Aqueous Solutions[1]

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Water and chloride ion exchange rates have been measured in concentrated aqueous solutions containing nickel(II). The measured exchanges proceed independently in the temperature range studied. Both chloride and perchlorate ions increase the water exchange rate in nickel aquo species. Kinetic results and scalar coupling constants are given.

Introduction

Studies on water and other ligand exchanges for labile systems can be expected to yield more insight into the detailed processes occurring in aqueous solutions. We have previously reported on the Ni(II)–H_2O–NCS^- system[3] where it was found that water and thiocyanate exchange proceeded independently. Zeltman and Morgan[4] studied water and chloride exchange in iron(III)–chloride systems and suggested that different iron species are responsible for the observed water and chloride exchanges. The work reported here is in continuation of our general studies on such reaction.

Experimental Section

For the most part, techniques and equipment previously described[3] have been used. Using a static field of 9270 G, the ^{35}Cl nmr line in LiCl or HCl solutions was observed at 3.88 Mc/sec, and the ^{17}O line in water, at 5.35 Mc/sec. Both square-wave modulation[3] and side-band techniques[5] were used in observing the resonances. The agreement between these techniques was satisfactory. Some experiments were done at lower fields to check on field effects.

Solutions were prepared using water containing 1.19 atom % ^{17}O (*ca.* 17% ^{18}O and normal H content) obtained from Bio-Rad Laboratories. This water was redistilled *in vacuo*. Reagents used were Mallinckrodt Analytical reagent $NiCl_2 \cdot 6H_2O$ and 36% HCl, Baker and Adamson reagent LiCl, and Merck reagent $LiClO_4$ recrystallized from water.

Measurements of ^{35}Cl chemical shifts were made relative to 70% $HClO_4$ contained in a small, sealed ampoule placed inside the usual sample tube.

Treatment of Data and Results

The treatment of data follows the discussion given earlier.[3,5] We are concerned here with line broadenings of free $H_2{}^{17}O$ and $^{35}Cl^-$ nmr absorption signals and paramagnetic shifts of the $^{35}Cl^-$ line produced by Ni(II) addition. Under the conditions of our experiments no shifts (>30 ppm) in the $H_2{}^{17}O$ lines were observed. Line-broadening results are reported in terms of the quantity $T_{2p}'' \equiv 2m(\text{Ni})/\gamma\Delta'$, where m(Ni) is the total molality of Ni(II), γ is the relevant magnetogyric ratio (3628 G^{-1} sec^{-1} for ^{17}O and 2620 G^{-1} sec^{-1} for ^{35}Cl), and Δ' is the line broadening in gauss, measured at half-maximum absorption using the full line widths, produced by Ni(II). That is, Δ' is $(W_{\text{obsd}} - W_0)$ where W_{obsd} is the line width at half-maximum absorption observed for the free ligand in the presence of Ni(II) and W_0 is the same quantity observed under identical conditions but in the absence of Ni(II). The data are given in Tables I–IV. Values of Δ' are the average of three or four measurements and have a precision of ±5–10%. In Figures 1 and 2 are shown semilogarithmic plots of T_{2p}'' *vs.* $10^3/T$, where T is the absolute temperature.

The shift data for ^{35}Cl are given in Table V and the function $TSm(\text{Cl}^-)t/m(\text{Ni})$ *vs.* $10^3/T$ is plotted in Figure 1. Here S is referred to the ^{35}Cl nmr frequency in HCl or LiCl solutions in the absence of Ni(II) and is the change in frequency produced by the addition of Ni(II) divided by the original frequency. The term $m(\text{Cl}^-)t$ is the *total chloride* molality in solution.

The chloride results are essentially the same in LiCl and HCl solution and are treated as such. The line-broadening mechanism is most likely mainly due to quadrupole relaxation effects on the ^{35}Cl nucleus. Line broadenings were measured at 9270 and 6000 G. At the lower field T_{2p}'' increased only by a factor of 1.3 or less near the T_{2p}'' minimum whereas factor of 2.4 is expected if the change in precessional frequency ($\Delta\omega$ mechanism) dominates the line broadening produced.[5] The values of T_{2p}'' on the right-hand portion of the curve in Figure 1 in either case ($\Delta\omega$ or quadrupole relaxation) approach τ_L which is the mean lifetime for exchange of a free Cl^- with a bound Cl^- in some Ni(II) species. The quantity τ_L is equal to $[\text{Cl}^-(\text{free})]/R$ where R is the exchange rate. From values of T_{2p}'' on the right-hand asymptotic line we calculate the rates and activation energy. The results are given in Table VI.

The ^{35}Cl chemical shifts observed are most simply explained by assuming the presence of a relatively minor, more rapidly exchanging species for which the scalar coupling process is more important. Discussion of possible species is deferred to a later section.

The water-exchange data appear to be most consistent with a $\Delta\omega$ mechanism for line broadening, but this cannot be decided with much certainty in the absence of measurable shifts and with the poor signal to noise ratios obtained at lower magnetic fields. The low-temperature data again are reasonable for ex-

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Table I

Line-Broadening Data for Cl^- Exchange in 7.8 *m* LiCl (6.7 *M*)

Temp, °C	Δ′, G	$10^5T_{2p}''$, *m* sec	W_0, G	Temp, °C	Δ′, G	$10^5T_{2p}''$, *m* sec	W_0, G
(A) 0.236 *m* Ni				(B) 0.358 *m* Ni			
21.4	1.09	16.6	0.19	10.6	0.96	28.5	0.21
29.4	1.26	14.3	0.21	71.6	1.30	21.0	0.24
38.9	1.24	14.5	0.21	90.8	1.34	20.4	0.23
45.0	1.06	17.0	0.21				
49.4	0.99	18.2	0.19	(D) 1.17 *m* Ni			
62.9	0.86	21.0	0.21	−27.6	0.62	143	0.41
71.6	0.77	23.3	0.24	−25.9	0.62	145	0.42
82.9	0.70	24.6	0.20	−19.6	0.72	124	0.31
90.8	0.70	25.7	0.23	−12.1	0.99	90	0.25
(C) 0.587 *m* Ni				−5.4	1.35	66	0.24
−5.4	0.62	72.4	0.24				
2.8	1.02	44.2	0.27				
10.6	1.90	23.6	0.21				

Table II

Line-Broadening Data for Cl^- Exchange in 7.8 *m* HCl (6.7 *M*)

Temp, °C	Δ′, G	$10^5T_{2p}''$, *m* sec	W_0, G	Temp, °C	Δ′, G	$10^5T_{2p}''$, *m* sec	W_0, G
(A) 0.230 *m* Ni				(B) 0.367 *m* Ni			
12.3	1.09	16.4	0.29	0.0	0.74	37.8	0.26
15.6	0.99	17.6	0.22	4.0	0.91	30.8	0.26
20.1	1.22	14.4	0.21	4.7	1.00	28.0	0.24
24.0	1.08	16.1	0.24	8.9	1.17	23.4	0.24
37.9	0.93	18.8	0.21	10.8	1.51	18.6	0.23
45.0	0.94	18.6	0.21	15.6	1.76	15.9	0.22
49.4	0.84	20.9	0.19	19.9	1.87	15.0	0.19
62.9	0.71	24.7	0.21	25.3	1.89	14.8	0.23
71.6	0.66	26.6	0.24	31.2	1.95	14.4	0.20
82.9	0.76	23.1	0.20	37.9	1.63	17.2	0.21
90.8	0.76	23.0	0.23	42.0	1.68	16.7	0.22
				45.0	0.94	18.9	0.21
(C) 0.580 *m* Ni				49.4	1.62	17.3	0.19
−11.2	0.64	68.9	0.27	62.9	1.25	22.4	0.21
−7.0	0.85	52.3	0.20	82.9	1.20	23.5	0.20
−1.5	1.38	32.1	0.29	90.8	1.15	24.4	0.23
14.4	2.62	16.9	0.23				
(D) 1.18 *m* Ni							
−14.8	0.79	114.2	0.33				
−11.9	0.93	96.3	0.35				
−4.6	1.63	55.1	0.32				
−1.2	1.98	45.3	0.29				

Table III

Line-Broadening Data for H_2O Exchange in 6.6 *m* LiCl (5.7 *M*)

Temp, °C	Δ′, G	$10^5T_{2p}''$, *m* sec	W_0, G	Temp, °C	Δ′, G	$10^5T_{2p}''$, *m* sec	W_0, G
(A) 0.0251 *m* Ni				(B) 0.0538 *m* Ni			
67.9	0.32	4.2	0.25	37.3	0.50	6.0	0.29
58.8	0.39	3.6	0.26	49.9	0.65	4.6	0.24
43.1	0.29	4.9	0.27	60.5	0.73	4.1	0.27
				75.2	0.59	5.1	0.19
(C) 0.119 *m* Ni				77.8	0.43	6.9	0.21
11.0	0.39	16.8	0.42	83.0	0.45	6.6	0.20
22.8	0.68	9.3	0.36	88.8	0.45	6.6	0.18
30.9	0.93	7.1	0.28				
37.5	1.08	6.1	0.27	(D) 0.271 *m* Ni			
				−15.2	0.29	51	0.77
				−11.9	0.33	45	0.70
				−3.6	0.48	32	0.59
				4.3	0.56	27	0.36

Table IV

Line-Broadening Data for H_2O Exchange in 6.5 *m* $LiClO_4$ (4.6 *M*)

Temp, °C	Δ′, G	$10^5T_{2p}''$, *m* sec	W_0, G
(A) 0.0257 *m* Ni			
71.8	0.35	4.2	0.26
83.8	0.38	3.7	0.23
(B) 0.0571 *m* Ni			
35.5	0.31	10.1	0.24
39.1	0.34	9.2	0.23
41.1	0.36	8.8	0.24
46.0	0.44	7.3	0.22
55.1	0.62	5.1	0.22
76.8	0.75	4.2	0.22
86.6	0.61	5.2	0.24
91.9	0.65	5.3	0.22
94.5	0.59	5.3	0.22

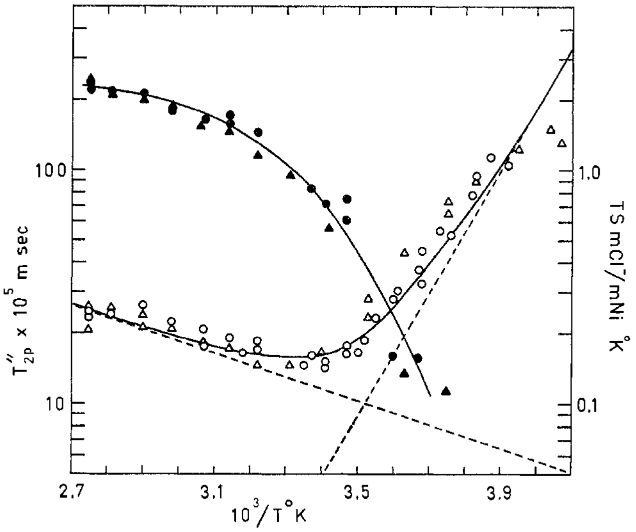

Figure 1.—Plot of T_{2p}'' *vs.* $10^3/T$ and $TSm(Cl^-)/m(Ni)$ *vs.* $10^3/T$ for $^{35}Cl^-$: open symbols, T_{2p}''; solid symbols, shifts; Δ, LiCl data; O, HCl data. The dashed lines are those used in the curve-fitting procedure.

change-controlled line broadening. The $H_2{}^{17}O$ data were obtained in solutions 6.6 *m* and 7.8 *m* in LiCl. No significant concentration effect was noted. The solubility behavior of $LiClO_4$ prevented using concentrations higher than 6.5 *m*. The kinetic results are given in Table VI. Assuming that the Δω mechanism applies to the water data, we calculate approximate scalar coupling constants (A/h) for the Ni(II)–H_2O interactions from the T_{2p}'' values at the intersection point of the asymptotic lines[3] and these are given in Table VI.

Discussion

The problem of identification of Ni(II) species in aqueous chloride solutions has received considerable attention.[6–12] It would appear from the work reported that our solutions may contain $NiCl^+$ and $NiCl_2$ complexes, but probably not higher ones. The equilibrium constants appear to be small and uncertain. Equilibria for the lower complexes seem not to be affected much by temperature ($\Delta H \cong 0.5$ kcal/mole[10]).

The ^{35}Cl line-broadening data and shifts and their temperature dependences are not all explainable in

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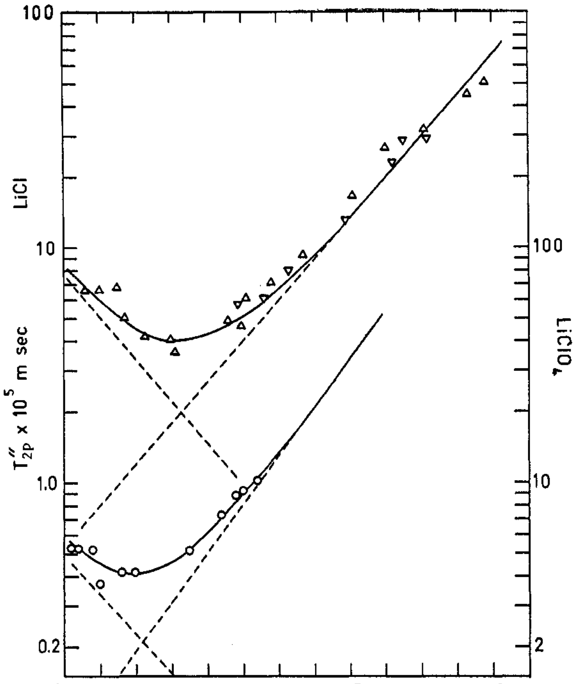


Figure 2.—Plot of T_{2p}'' vs. $10^3/T$ for $H_2{}^{17}O$: ▽, 7.8 *m* LiCl; △, 6.6 *m* LiCl; ○, 6.5 *m* $LiClO_4$. The right-hand scale applies to the $LiClO_4$ data.

TABLE V

CHEMICAL SHIFT DATA FOR ^{35}Cl IN CHLORIDE SOLUTIONS

[Ni], *m*	Temp, °C	Shifts (*S*), ppm	*TSm*-$(Cl^-)_t/m$ (Ni)	[Ni], *m*	Temp, °C	Shifts (*S*), ppm	*TSm*-$(Cl^-)_t/m$ (Ni)
(A) 7.8 *m* HCl				(B) 7.8 *m* LiCl			
0.229	15.8	96	0.75	0.236	21.6	56	0.56
0.229	20.3	70	0.71	0.236	29.6	93	0.95
0.229	24.3	81	0.84	0.236	38.1	108	1.14
0.229	38.1	137	1.47	0.236	45.2	133	1.44
0.229	45.2	156	1.72	0.236	49.7	142	1.55
0.229	49.7	147	1.64	0.236	63.1	160	1.82
0.229	63.1	155	1.80	0.236	71.8	170	1.99
0.229	91.0	187	2.35	0.236	83.1	174	2.10
0.229	71.8	176	2.10	0.236	91.0	297	2.41
0.229	83.1	174	2.14	0.358	10.8	35	0.23
0.367	0.25	26	0.16	0.358	91.0	297	2.42
0.367	4.90	26	0.16	0.587	−5.3	31	0.11
0.367	15.8	96	0.60	0.587	3.1	36	0.14
0.367	45.2	230	1.60	0.587	10.8	59	0.23
0.367	49.7	233	1.65	1.17	−5.3	59	0.11
0.367	91.0	277	2.20				

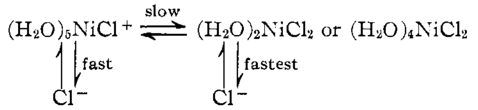
terms of a single chloro complex of nickel; *i.e.*, the absence of a large field effect on the line broadenings and the low slope of T_{2p}'' vs. $10^3/T$ at high temperatures cannot be reconciled with the relatively large chemical shifts observed. Using the two-site equations of Swift and Connick[5] and the observed chemical shifts, the calculated T_{2p}'' values near the minimum are about half the observed values. Any additional relaxation processes could only make the calculated T_{2p}'' values smaller and therefore the discrepancy between observed and calculated T_{2p}'' values larger. The simplest explanation consistent with the observations and calculations seems to be that two different chloro complexes are present with one being responsible for the observed shift and the other responsible for the broadening. The results can be simply, though not uniquely, rationalized in terms of the scheme

TABLE VI

KINETIC DATA FOR 1 *m* Ni(II) SOLUTIONS

System	Rate, *M* sec^{-1}	E_a, kcal/mole	*A/h*, cps
7.8 *m* HCl or LiCl	1.8×10^5 (25°)	12 ± 1	. . .
Cl^- exchange	1.2×10^4 (−10°)		
6.6–7.8 *m* LiCl	6.9×10^5 (25°)	8.0 ± 1	3.5×10^7 ($5H_2O$/Ni)
H_2O exchange	1.1×10^5 (−10°)		
6.5 *m* $LiClO_4$	2.5×10^5 (25°)	9.6 ± 1	2.8×10^7 ($6H_2O$/Ni)
H_2O exchange	2.8×10^4 (−10°)		
0.1 *M* $HClO_4$	1.6×10^5 (25°)	11.6[a]	4.3×10^{7a} ($6H_2O$/Ni)
H_2O exchange		10.8[b]	3.0×10^{7b} ($4H_2O$/Ni)
			1.9×10^7 ($6H_2O$/Ni)

[a] T. W. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962). [b] R. E. Connick and D. E. Flat, *ibid.*, **44**, 4103 (1966).



$$\begin{tikzcd}(H_2O)_5NiCl^+ \arrow[r, shift left, "slow"] \arrow[d, shift left, "fast"] & (H_2O)_2NiCl_2 \text{ or } (H_2O)_4NiCl_2 \arrow[l, shift left] \arrow[d, shift left, "fastest"] \\ Cl^- \arrow[u, shift left] & Cl^- \arrow[u, shift left]\end{tikzcd}$$

The observed line broadenings are then due to Cl^- exchange with $NiCl^+$ while the shifts arise in the more rapid exchange of Cl^- and $NiCl_2$. The interconversion of the chloro complexes needs to be relatively slow, and perhaps a change in coordination number would help to meet this requirement. If *ca.* 10% $NiCl_2$ were present with an exchange rate *ca.* a factor of 10 greater than for $NiCl^+$ and an *A/h* value of *ca.* 5×10^7 cps, the data could be accounted for. The *A/h* value seems reasonable at least for a tetrahedral Ni(II) species in the absence of direct evidence. The line broadenings observed are probably due to quadrupolar interactions with an apparent "activation energy" of *ca.* −2.3 kcal/mole, and the implication is that the scalar coupling is less for the $NiCl^+$ species than for $NiCl_2$.

A comparison of water-exchange rates (Table VI) in the various systems listed is of some interest. Addition of $LiClO_4$ or LiCl to the aquonickel system produces an increase of water-exchange rate and a lowering of activation energy with LiCl the more effective solute. To what extent these results should be ascribed to general or specific salt effects is impossible to say at present. One can say that the observed chloride and water exchanges in LiCl proceed independently with the water exchange more rapid at low temperatures (*ca.* a factor of 10) and with a lower activation energy. The studies[3,4] on Fe(III)–Cl^-, Ni(II)–NCS^-, and the present system all show that simple coupled mechanisms of the sort $M(H_2O)_x{}^{z+} + L \rightleftharpoons [M(H_2O)_{x-1}L]^{z+} + H_2O$ alone will not account for water- and ligand-exchange results. In such cases at least the relation between ligand substitution and water exchange is complex, and much more information is needed before mechanisms can be identified.

In order to obtain more definitive results, higher precision is needed for the measurements. Variation of solution composition is suggested, and the salt effects on water exchange should be looked at in more detail. With improved equipment it may be possible to detect the shifted lines in the complex species responsible for the observed effects.

The scalar coupling constants obtained for the Ni–H_2O interactions (Table VI) are similar to those reported for more dilute solutions containing aquonickel ions. Our values are, however, somewhat higher than the more recent ones. This suggests that Connick and Fiat's[13] report of four-coordination for the Ni(II) aquo ion may be at least partly a consequence of the high salt concentration used in their direct shift measurements.

[13] R. E. Connick and D. E. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

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Magnetic Exchange in Transition Metal Complexes. IV.[1a] Linear Trimeric Bis(acetylacetonato)nickel(II)

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The magnetic properties of the linear trimeric cluster $[Ni_3(acac)_6]$ have been measured from room temperature (296°K) down to 0.365°K. At room temperature, the normal value of 3.23 BM per Ni^{2+} ion is found for the effective magnetic moment corresponding to octahedrally coordinated nickel(II). As the temperature is lowered, μ_{eff} (corrected for a small Curie–Weiss constant, $\theta = -0.2°$, due to weak lattice antiferromagnetism) increases monotonically until a constant value of 4.1 ± 0.1 BM is reached below about 10°K. These results, together with magnetization curves at 1.6 and 4.2°K, demonstrate that the six e_g electrons on the three Ni atoms are ferromagnetically coupled, the ground molecular spin state for the trimer being $S = 3$ (*i.e.*, six spins parallel). Comparison of our results with an extension of Kambe's theory for the susceptibility of a magnetically isolated exchange-coupled trimer indicates that adjacent Ni atoms in the linear triad have the positive coupling constant $J = +37°$ ($\equiv +26$ cm^{-1}) while the terminal Ni atoms have the negative value $J_{31} = -10.3°$ ($\equiv -7$ cm^{-1}). The opposing signs for these interactions are shown to be consistent with current views of superexchange. Nickel(II) acetylacetonate provides the first example of ferromagnetic interaction in an isolated cluster.

Introduction

Bis(acetylacetonato)nickel(II) provides an extremely interesting example of a compound in which the crystal lattice is built up of magnetically isolated linear triads of transition metal atoms, with two unpaired e_g spins per atom. Theoretical considerations suggest that the magnetic properties of such an arrangement of unpaired spins might exhibit at least two novel features not previously observed in an isolated cluster complex: (1) There can be two different, nonzero, exchange integrals for a linear trimer molecule, one between adjacent metal atoms and the other between the terminal atoms. (2) The exchange integral between the adjacent Ni atoms may be positive (ferromagnetic).

Our measurements show that the magnetic susceptibility of $[Ni_3(acac)_6]$ is indeed characterized by both of these features.[2]

The structure[3] of $[Ni_3(acac)_6]$ is shown in Figure 1. Nearly octahedral coordination of each nickel ion in the linear trimeric molecule results from the sharing of triangular faces of adjacent octahedra. An acetylacetonato oxygen is situated at each apex of the linear triad of fused octahedra. The intramolecular Ni–Ni distances are 2.882 and 2.896 Å. There are no atomic bridges between molecules in the crystal lattice, and the closest intermolecular Ni–Ni distance is ~8 Å. Consequently, intermolecular spin–spin coupling due to both exchange and dipole–dipole forces is expected to be very weak. The trimer molecules should behave as if magnetically isolated from each other at all but the very lowest temperatures.

Theory

We shall discuss the magnetic susceptibility of $[Ni_3(acac)_6]$ in terms of the usual Heisenberg–Dirac–Van Vleck spin-coupling Hamiltonian first used by Kambe[4] for this purpose. For an isolated linear trimer, this Hamiltonian is

$$H = -2J[(\hat{S}_1\cdot\hat{S}_2) + (\hat{S}_2\cdot\hat{S}_3)] - 2J_{31}(\hat{S}_3\cdot\hat{S}_1) \qquad (1)$$

J is the exchange integral between adjacent nickel atoms (1,2 and 2,3) in the trimer, and J_{31} is the exchange integral between the two terminal nickel atoms (3,1) within the trimer. The $\hat{S}_i$ are spin angular momentum operators. For a system with two unpaired spins on each metal atom, the eigenvalues of (1) are given in Table I, where S' is the total spin of the trimer and S^* is the total spin of the two terminal atoms.[4] Figure 2, which may be referred to as a spin-correlation diagram, shows how the ordering of the spin levels depends on the sign of J and J_{31} and on their relative magnitudes. The diagram is drawn for

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